University of Alberta

Mono- and Binuclear Metallacyclic Complexes: Synthesis, Reactivity, and Mechanism of Formation

by

Tian-Fu Mao ©

A thesis
submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

Department of Chemistry

Edmonton, Alberta
Fall, 1996

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-612-18078-6

Canada

University of Alberta

Release Form

Name of Author: Tian-Fu Mao

Title of Thesis: Mono- and Binuclear Metallacyclic Complexes: Synthesis, Reactivity, and Mechanism of Formation

Degree: Doctor of Philosophy

Year this Degree Granted: 1996

Permission is hereby granted to the University of Alberta Library to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly, or scientific research purposes only.

The author reserves all other publication and other rights in association with the copyright in the thesis, and except as hereinbefore provided, neither the thesis nor any substantial portion thereof may be printed or otherwise reproduced in any material form whatever without the author's prior written permission.

(Signed)____________________

#17, 10910 - 53 Ave.
Edmonton, Alberta
T6H 0S3

Date: June 19 , 1996

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Mono- and Binuclear Metallacyclic Complexes: Synthesis, Reactivity, and Mechanism of Formation** submitted by Tian-Fu Mao in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

J. Takats (Supervisor)

steven Bergens

S. H. Bergens

RGCavell

R. G. Cavell

S. Kresta

R. E. D. McClung

R. J. Puddephatt

Date: June 18 , 1996

To my parents, my wife Li, and my daughter Angela

Abstract

A variety of mononuclear and dinuclear metallacyclic complexes were synthesized by reaction of $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) complexes with classical and nonclassical nucleophiles. The reactivity of the resulting metallacycles and the mechanism of their formation were also investigated.

The reactions of $M(CO)_4(\eta^2\text{-alkyne})$ with monophosphines (PMe_3, PPh_3, $P(^tBu)_3$) are strongly dependent on the alkyne employed. For electron poor alkynes, the reactions give both monosubstituted and disubstituted products, $Os(CO)_3(PMe_3)(\eta^2\text{-}RC_2R')$ (R = R' = CF_3, **2a**; R = H, R' = CF_3, **2b**), $Os(CO)_3(PPh_3)(\eta^2\text{-HFB})$ (**2c**), $Ru(CO)_3(PMe_3)(\eta^2\text{-HFB})$ (**2d**), $Os(CO)_3(PMe_3)(\eta^2\text{-}C_2H_2)$ (**2f**), $Os(CO)_2(PMe_3)_2(\eta^2\text{-}RC_2R')$ (R = R' = CF_3, **3a**; R = H, R' = CF_3, **3b**), $Os(CO)_2(PPh_3)_2(\eta^2\text{-HFB})$ (**3c**), and $Ru(CO)_2(PR''_3)_2(\eta^2\text{-HFB})$ (R" = Me, **3d**; R" = Ph, **3e**). In the case of electron rich alkynes, on the other hand, the reactions generate both CO substitution and CO insertion products, $Os(CO)_2(PMe_3)_2(\eta^2\text{-}C_2H_2)$ (**3f**), $Os(CO)_2(PMe_3)_2\{\eta^2\text{-}C_2H_2C(O)\}$ (**4a**, **4b**), and $Os(CO)_3\{P(^tBu)_3\}\{\eta^2\text{-}C(O)C_2R_2C(O)\}$ (R = Me, **5a**; H, **5b**). While most of these compounds are stable at room temperature, compounds **2f** and **3f** undergo further transformation. Compound **3f** undergoes an oxidative addition reaction to yield $Os(CO)_2(PMe_3)_2(H)(C_2H)$ (**6**), whereas **2f** forms a novel dimetallacyclic compound $Os_2(CO)_5(PMe_3)_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2H_2C(O)C_2H_2\}$ (**7**).

The reaction of $Os(CO)_4(\eta^2\text{-}C_2R_2)$ (R = H, Me) with dppm (bis(diphenylphosphino)methane) results in the formation of an osmacyclobutenone, $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (**10a** and **10b**), or an osmacyclopentenedione, $Os(CO)_2\{\eta^2\text{-}C(O)CMeCMeC(O)\}(\eta^2\text{-dppm})$ (**12**),

depending on the alkyne. Low temperature NMR studies show that species **10a** and **10b** are formed through the intermediacy of $Os(CO)_3(\eta^2\text{-}C_2H_2)(\eta^1\text{-}dppm)$ (**11**). The reactions of $Ru(CO)_4(\eta^2\text{-}HFB)$ with dppm and dmpm (bis(dimethylphosphino)methane) generate the metallacyclic compounds $(OC)_3Ru\text{-}P(R_2)(CH)\text{-}P(R_2)\text{-}C(CF_3)\text{-}C(H)(CF_3)$ (R = Ph, **8a**; Me, **8b**) whereas its reactions with dppe (bis(diphenylphosphino)ethane) and dmpe (bis(dimethylphosphino)ethane) give the disubstituted products $Ru(CO)_2(\eta^2\text{-}R_2P(CH_2)_2PR_2)(\eta^2\text{-}HFB)$ (R = Ph, **9a**; R = Me, **9b**).

The reactions of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with $M''(CO)_4(\eta^1\text{-}dppm)$ (M" = Fe, Ru) yield dimetallacyclopentenones, $OsRu(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}CHCHC(O)\}(\mu\text{-}dppm)$ (**13**) and $FeOs(CO)_6(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_2C(O)\}(\mu\text{-}dppm)$ (**18**), whereas the reaction of $Ru(CO)_4(\eta^2\text{-}HFB)$ with $Fe(CO)_4(\eta^1\text{-}dppm)$ gives the dimetallacyclobutene $FeRu(CO)_6(\mu\text{-}\eta^1\text{:}\eta^1\text{-}HFB)(\mu\text{-}dppm)$ (**20**). Low temperature NMR monitoring shows that compound **13** is formed via the intermediates $RuOs(CO)_7(\eta^2\text{-}C_2H_2)(\mu\text{-}dppm)$ (**16**), $OsRu(CO)_6\{\eta^2\text{-}C_2H_2C(O)\}(\mu\text{-}dppm)$ (**17**), and $OsRu(CO)_6\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_2C(O)\}(\mu\text{-}dppm)$ (**15**). An intermediate, $FeOs(CO)_7(\eta^2\text{-}HFB)(\mu\text{-}dppm)$, is also observed in the formation of compound **20**.

The reaction of complex **10a** with $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ and $CpRh(CO)_2$ generate the corresponding dimetallacyclopentenone species **13** and $CpRhOs(CO)_3\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_2C(O)\}(\mu\text{-}dppm)$ (**14**). Complexes **10a** and **12** react with methyl triflate to yield the Fisher-type carbene complexes $[Os(CO)_2\{\eta^2\text{-}CHCHC(OMe)\}(\eta^2\text{-}dppm)][SO_3CF_3]$ (**22**) and $[Os(CO)_2\{\eta^2\text{-}C(O)CMeCMeC(OMe)\}(\eta^2\text{-}dppm)][SO_3CF_3]$ (**23**). The thermolysis of compound **13** generates a novel compound $OsRu(CO)_5\{(\mu-PPh_2PCH_2P(Ph)C_6H_4CMe\}$ (**24**).

The molecular structures of compounds **8a**, **10a**, **12**, and **13** have been determined by single crystal X-ray crystallography.

Acknowledgements

The work presented could not have been accomplished without the help and support of many people. I would like to take this opportunity to express my sincere appreciation to them.

First, and foremost, I would like to thank my supervisor, Professor Josef Takats, for his guidance, encouragement, enthusiasm, and friendship.

I would also like to extend my thanks to Professor John L. Falconer for his encouragement and friendship.

I am grateful to the members of Professor Takats' research group for their assistance and friendship. In particular, Jason Cooke, John Washington, Ken Hoffmann, Xingwang Zhang, Yimin Sun, Wenyi Fu, Jean Pearson, and Zhongsheng Zhang.

I would like to thank the NMR staff including Dr. Tom Nakashima, Glen Bigam, Tom Brisbane, Gerdy Aarts and Lai Kong for their talented assistance in obtaining numerous NMR spectra. The efforts of Darlene Mahlow and Andrea Dunn for elemental analysis and Drs. Bob McDonald, Andrew Bond, Robin Rogers, and Victor W. Day for X-ray structure determinations are gratefully acknowledged.

Special thanks go to my wife Li for her love, understanding, and support; my daughter, Angela, for much joy she has brought into my family; my parents for their prayers for my success.

Finally, I wish to thank other members of my family and friends both here and overseas for their encouragement and support.

Table of Contents

Chapter 1

Introduction

1.1 Survey of Metallacyclic Complexes 1

  1.1.1 Mononuclear Metallacyclic Complexes 1

  1.1.2 Binuclear Metallacyclic Complexes 5

1.2 $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) Complexes 12

1.3 Scope of the Thesis 21

1.4 References 26

Chapter 2

Reactions of $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) with Monophosphines

2.1 Introduction 35

2.2 Results and Discussion 36

  2.2.1 Reactions of $M(CO)_4(\eta^2\text{-}RC_2R')$ (M = Ru, R = R' = CF_3; M = Os, R = R' = CF_3; R = H, R' = CF_3) with PR''_3 (R'' = Me, Ph) 36

  2.2.2 Reactions of $Os(CO)_4(\eta^2\text{-}RC_2R)$ (R = H, Me) with PR'_3 (R' = Me, ^{t}Bu) 43

  2.2.3 Pathways for CO Substitution and Insertion Processes 48

  2.2.4 Thermal Stability of Phosphine Adducts 55

2.3 Conclusions 64

2.4 Experimental Section 66

  2.4.1 Solvents and General Techniques 66

  2.4.2 Physical Measurements 67

2.4.3 Photochemical Techniques 67
2.4.4 Starting Materials and Reagents 69
2.4.5 Synthetic Procedures 70
2.5 References 81

Chapter 3

Reactions of $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) with Diphosphines

3.1 Introduction 86
3.2 Results and Discussion 87
3.2.1 Reactions of $Ru(CO)_4(\eta^2\text{-}F_3CC_2CF_3)$ with dppm and dmpm 87
3.2.2 Reactions of $Ru(CO)_4(\eta^2\text{-}F_3CC_2CF_3)$ with dppe and dmpe 94
3.2.3 Reactions of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with dppm 97
3.2.4 Reactions of $Os(CO)_4(\eta^2\text{-}C_2Me_2)$ with dppm 106
3.3 Conclusions 114
3.4 Experimental Section 116
3.4.1 Starting Materials and Reagents 116
3.4.2 Synthetic Procedures 116
3.4.3 X-ray Structure Determination of **8a** 121
3.4.4 X-ray Structure Determination of **10a** 122
3.4.5 X-ray Structure Determination of **12** 131
3.5 References 136

Chapter 4

The Role of Metallacyclobutenone in the Formation of Dimetallacyclopentenone Complexes

4.1 Introduction 139

4.2 Results and Discussion 141

  4.2.1 Reaction of $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (10a) with $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ 141

  4.2.2 Reaction of $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (10a) with $CpRh(CO)_2$ 148

4.3 Conclusions 152

4.4 Experimental Section 153

  4.4.1 Starting Materials and Reagents 153

  4.4.2 Synthetic Procedures 153

4.5 References 156

Chapter 5

Reaction of $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) with $M'(CO)_4(\eta^1\text{-dppm})$ (M' = Fe, Ru)

5.1 Introduction 160

5.2 Results and Discussion 161

  5.2.1 Reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with $M(CO)_4(\eta^1\text{-dppm})$ (M = Fe, Ru) 161

  5.2.2 Reaction of $Ru(CO)_4(\eta^2\text{-}CF_3C_2CF_3)$ with $Fe(CO)_4(\eta^1\text{-dppm})$ 174

5.3 Conclusions 179

5.4 Experimental Section 181

  5.4.1. Starting Materials and Reagents 181

5.4.2. Synthetic Procedures 181
5.5 References 185

Chapter 6

Reactivity of Metallacycles

6.1 Introduction 188
6.2 Results and Discussion 190
6.2.1 Alkylation of $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (**10a**) and $Os(CO)_2\{\eta^1,\eta^1\text{-}C(O)C(Me)C(Me)C(O)\}$ $(\eta^2\text{-dppm})$ (**12**) 190
6.2.2 Thermolysis of $RuOs(CO)_5\{\mu\text{-}\eta^1:\eta^3\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ 193
6.3 Conclusions 199
6.4 Experimental Section 200
6.4.1 Starting Materials 200
6.4.2 Synthetic Procedures 200
6.5 References 204

Chapter 7

Conclusions

7.1 References 213

List of Tables

Chapter 1

Table 1.1 Selected Bond Distances for $Os(CO)_4(\eta^2-C_2H_4)$ and $Os(CO)_4\{\eta^2-C_2(SiMe_3)_2\}$ 18

Chapter 2

Table 2.1 Selected ^1H NMR Data for **4a** and **4b** 45
Table 2.2 IR Data for **7** and Related Compounds 59
Table 2.3 Selected ^1H NMR Data for **7** and Related Compounds with Coordinated Pentenone Double Bond 60
Table 2.4 Selected ^1H NMR Data for **7** and Related Compounds with Uncoordinated Pentenone Double Bond 60
Table 2.5 The ^1H - ^{13}C Shift-correlated 2D NMR Data for **7** 62
Table 2.6 Solvents and Drying Agents 66

Chapter 3

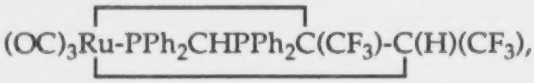
Table 3.1 Selected Bond Distances and Angles for

$(OC)_3Ru-PPh_2CHPPh_2C(CF_3)-C(H)(CF_3)$, **8a** 90
Table 3. 2 Selected ^1H NMR Data for **10b** 98
Table 3. 3 Selected Bond Distances and Angles for $Os(CO)_2\{\eta^2-C_2H_2C(O)\}(\eta^2-dppm)$, **10a** 102
Table 3.4 Selected Bond Distances and Angles for $Os(CO)_2\{\eta^2-C(O)CMeCMeC(O)\}(\eta^2-dppm)$, **12** 110
Table 3.5 Weighted Least-squares Plane Comprising Os-C(3)-C(4)-C(5)-C(6) 111

Table 3.6 Crystal Data and Summary of Data Collection and Structure Refinement for **8a** 123
Table 3.7 Final Fractional Coordinates for **8a** 125
Table 3.8 Crystal Data and Summary of Data Collection and Structure Refinement for **10a** 127
Table 3.9 Final Fractional Coordinates for **10a** 129
Table 3.10 Crystal Data and Summary of Data Collection and Structure Refinement for **12** 132
Table 3.11 Final Fractional Coordinates for **12** 134

Chapter 4

Table 4.1 IR Data for **13** and Related Compounds 142
Table 4.2 Selected ^{1}H NMR Data for **13** and Related Compounds 143
Table 4.3 Selected ^{13}C{^{1}H} NMR Data for **13** and Related Compounds 144
Table 4.4 IR Data for **14** and Related Compounds 149
Table 4.5 Selected ^{13}C{^{1}H} NMR Data for **14** and Related Compounds 150

List of Figures

Chapter 1

Figure 1.1 Common Types of Dimetallacycloalkenes 7

Figure 1.2 Bonding in Metal-alkyne Complexes 13

Figure 1.3 Interaction Diagram for $M(CO)_4(\eta^2\text{-alkyne})$ 15

Figure 1.4 Interaction Diagram for $Ir(PMe_2Ph)_3(\eta^2\text{-}C_2Me_2)^+$ 20

Chapter 2

Figure 2.1 Variable Temperature ^{19}F NMR Spectra 41

Figure 2.2 Molecular Structure of $Os(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2$ 51

Figure 2.3 Internal Photolysis Apparatus 68

Figure 2.3 External Photolysis Apparatus 69

Chapter 3

Figure 3.1 ORTEP View of
$(OC)_3Ru\text{-}PPh_2CHPPh_2C(CF_3)\text{-}C(H)(CF_3)$, **8a** 89

Figure 3.2 The $^{13}C\{^1H\}$ NMR Spectra of **10a** (top) and **10b** (bottom)
in the Carbonyl Region 100

Figure 3.3 ORTEP View of $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$, **10a** 101

Figure 3.4 $^{13}C\{^1H\}$ NMR Spectra of **12** in the Carbonyl Region 107

Figure 3.5 ORTEP View of
$Os(CO)_2\{\eta^2\text{-}C(O)CMeCMeC(O)\}(\eta^2\text{-dppm})$, **12** 109

Chapter 4

Figure 4.1 $^{13}C\{^1H\}$ NMR Spectrum of **13** in the Carbonyl Region 145

Chapter 5

Figure 5.1 ^{13}C and $^{13}C\{^1H\}$ NMR Spectra of compound **18** 165

Figure 5.2 $^{13}C\{^1H\}$ NMR Spectra of compound **15** 167

Figure 5.3 $^{31}P\{^1H\}$ NMR Monitoring of the Reaction of $Ru(CO)_4(\eta^1\text{-dppm})$ with $Os(CO)_4(\eta^2\text{-}C_2H_2)$: Formation of **13** 172

Chapter 6

Figure 6.1 $^{13}C\{^1H\}$ and $^{13}C\{^{31}P\}$ NMR Spectra of **24** 195

List of Schemes

Chapter 1

Scheme 1.1 6

Scheme 1.2 18

Chapter 2

Scheme 2.1 40

Scheme 2.2 44

Scheme 2.3 46

Scheme 2.4 49

Scheme 2.5 54

Scheme 2.6 55

Scheme 2.7 57

Scheme 2.8 58

Scheme 2.9 63

Scheme 2.10 63

Chapter 3

Scheme 3.1 91

Scheme 3.2 93

Scheme 3.3 96

Scheme 3.4 103

Scheme 3.5 105

Scheme 3.6 108

Scheme 3.7 112

Scheme 3.8 113

Chapter 4

Scheme 4.1 139
Scheme 4.2 147
Scheme 4.3 151

Chapter 5

Scheme 5.1 173
Scheme 5.2 178

Chapter 6

Scheme 6.1 192
Scheme 6.2 197
Scheme 6.3 199

List of Abbreviations and Symbols

Å	Angstrom(s)
Anal.	analytical
APT	attached proton test
atm	atmosphere(s)
br	broad
ca.	circa (approximately)
Calc.	calculated
Cp	cyclopentadienyl, C_5H_5
Cp*	pentamethylcyclopentadienyl, $C_5(CH_3)_5$
δ	chemical shift in ppm
d	doublet
dd	doublet of doublets
ddd	doublet of doublets of doublets
deg	degree(s)
dmpm	bis(dimethylphosphino)methane, $(CH_3)_2PCH_2P(CH_3)_2$
dmpe	bis(dimethylphosphino)ethane, $(CH_3)_2PCH_2CH_2P(CH_3)_2$
dppe	bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$
dppm	bis(diphenylphosphino)methane, $(C_6H_5)_2PCH_2P(C_6H_5)_2$
dq	doublet of quartets
E.I.	electron impact
esd	estimated standard deviation

eV	electron volts
FAB	fast atom bombardment
FT-IR	Fourier Transform Infrared
GWV	Glasswerk Wertheim
h	hour(s)
HFB	hexafluoro-2-butyne, $C_2(CF_3)_2$
$h\nu$	radiation
Hz	Hertz
J	coupling constant
K	Kelvin
LT	low temperature
λ	wavelength
m	multiplet (reference to NMR spectra)
m	medium (reference to IR spectra)
Me	methyl, CH_3-
mg	milligrams
min	minute(s)
MHz	megahertz
mL	milliliters
mmol	millimoles
mp	melting point
MS	mass spectrometry
nm	nanometers
NMR	nuclear magnetic resonance
ν	stretching frequency
Ph	phenyl, C_6H_5-
ppm	parts per million

q	quartet
s	singlet (with reference to NMR spectra)
s	strong (with reference to IR spectra)
t	triplet
^{t}Bu	tertiary-butyl, $C(CH_3)_3$-
TFP	trifluoropropyne, $HCC(CF_3)$
THF	tetrahydrofuran
μL	microliters
w	weak
v	very
VT	variable temperature

Chapter 1

Introduction

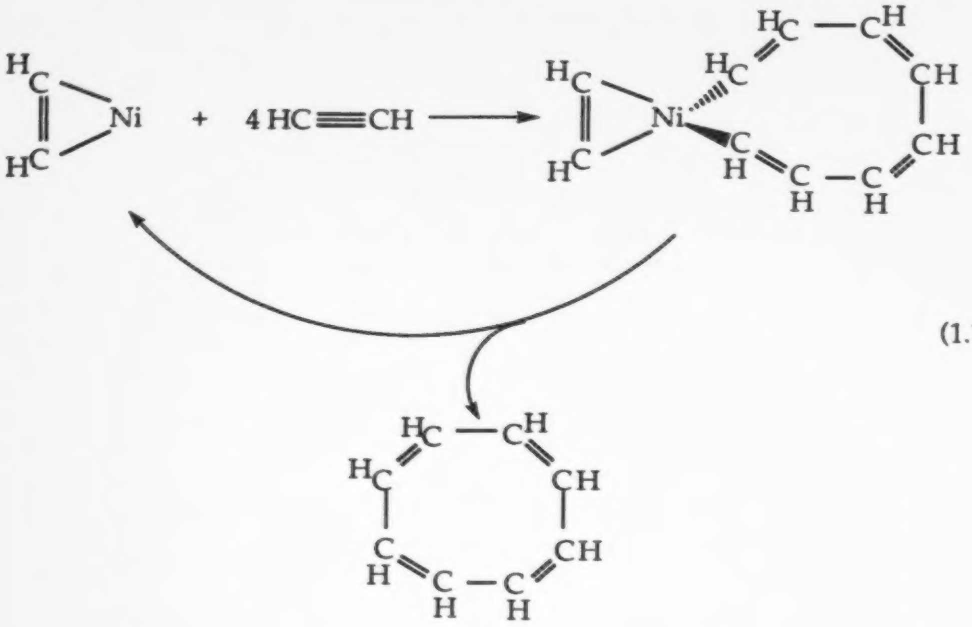
1.1 Survey of Metallacyclic Complexes

Metallacycles are compounds that have a ring containing at least one metal-carbon σ bond.[1,2] The area of metallacycle chemistry has developed rapidly during the last two decades. Interest in these complexes has arisen as a result of their recognized importance as reactive intermediates in many homogeneous transition metal-catalyzed organic transformations,[3-6] and as models for surface transformation in heterogeneous catalysis.[7-10] In particular, metallacycloalkanes are involved in numerous catalytic reactions such as alkene metathesis and oligomerization of olefins. This subject has been thoroughly studied and repeatedly reviewed[5,6,11,12] and will not be treated here.

For the purpose of this thesis, metallacycloalkenes and related complexes are of particular concern. Such complexes have also been implicated in numerous very important processes such as metal-induced alkyne metathesis, carbonylation, cyclotrimerization, oligomerization, and polymerization of alkynes.[1,2,13]

1.1.1 Mononuclear Metallacyclic Complexes

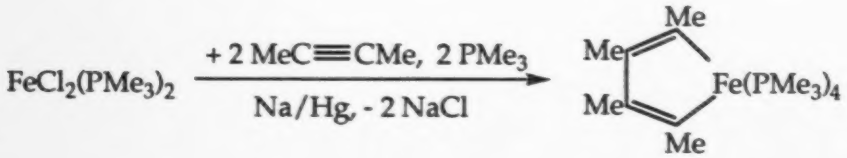
Walter Reppe, the "father" of metallacyclic chemistry, was the first to propose a metallacycle as an intermediate in the catalytic formation of cyclooctatetraene in 1948 (eq. 1.1).[14] Since then, much effort has been devoted to the synthesis of this class of complexes as it may be useful in elucidating the role they play in this and related catalytic processes.



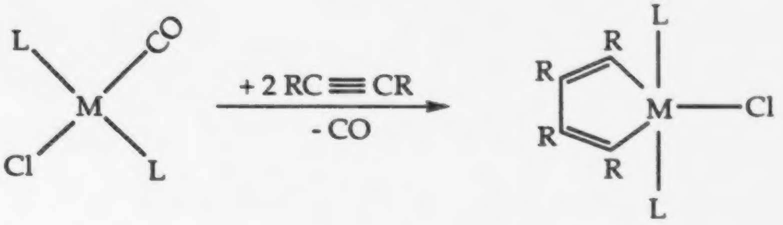
(1.1)

There are a variety of general methods that have been developed for the syntheses of transition metallacycloalkenes, they include: (1) coupling of bisalkyne or alkyne/alkene ligands; (2) carbonylation of alkyne metal complexes; (3) addition of alkynes to metal carbyne complexes; (4) metathesis reaction of metal halides with di-lithio and di-Grignard reagents.[1,15]

The vast majority of metallacycloalkene complexes have been obtained by transition metal mediated coupling of alkynes; this method often affords five-membered metallacyclopentadiene complexes (eqs. 1.2 - 1.5).[16-19]

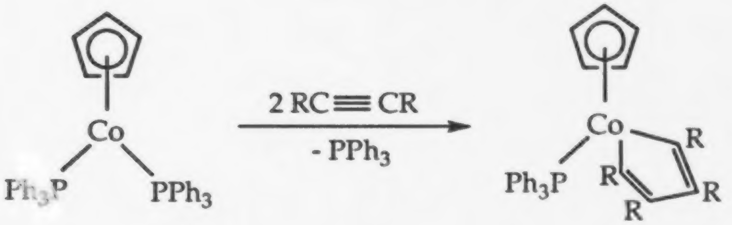

FeCl2(PMe3)2
+ 2 MeC≡CMe, 2 PMe3
Na/Hg, - 2 NaCl
Me
Me
Me
Me
Fe(PMe3)4

(1.2)


L
CO
M
Cl
L
+ 2 RC≡CR
- CO
R
R
R
R
L
M
Cl
L

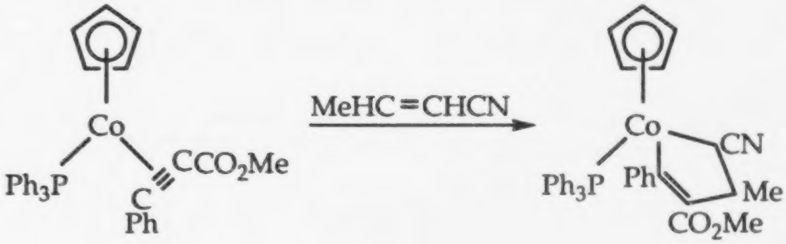
(1.3)

M = Ir, L = PPh_3, R = CO_2Me, CO_2Et.
M = Rh, L = $AsPh_3$, R = CO_2Me


Co
Ph3P
PPh3
2 RC≡CR
- PPh3
Co
Ph3P
R
R
R
R

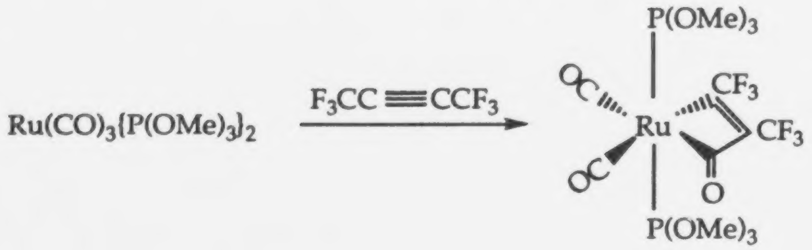
(1.4)

R = Ph, CO_2Me

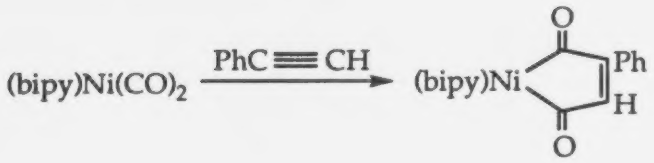

Co
Ph3P
CCO2Me
C
Ph
MeHC=CHCN
Co
Ph3P
Ph
CN
Me
CO2Me

(1.5)

Carbonylation reaction of alkynes promoted by transition metal complexes is very important in both industrial and laboratory organic synthesis.[20,21] Metallacyclobutenone or metallacyclopentenediones are obtained by carbonyl insertion into metal-alkyne bonds. However, examples of this type of transformation are rather limited (eqs. 1.6 - 1.7).[22-24]

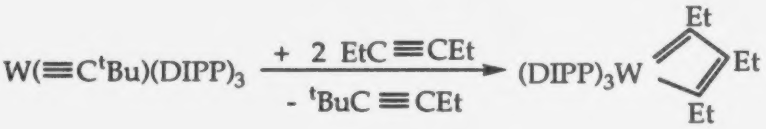

Ru(CO)3{P(OMe)3}2
F3CC≡CCF3
P(OMe)3
OC
OC
Ru
CF3
CF3
O
P(OMe)3

(1.6)


(bipy)Ni(CO)2
PhC≡CH
(bipy)Ni
O
Ph
H
O

(1.7)

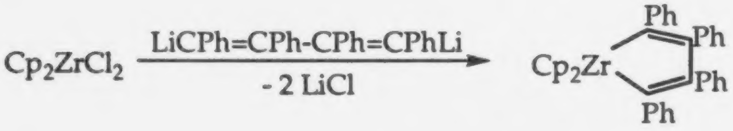
The reaction of alkylidyne complexes with alkynes gives metallacyclobutadienes. These complexes contain four-membered rings and are reactive intermediates in alkyne metathesis reactions (eq. 1.8).[25-28]


W(≡C^{t}Bu)(DIPP)3
+ 2 EtC≡CEt
- ^{t}BuC≡CEt
(DIPP)3W
Et
Et
Et

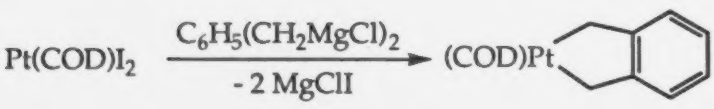
(1.8)

DIPP = O-2,6-$C_6H_3{}^iPr_2$

Treatment of transition metal halides with di-lithio or di-Grignard agents is another route to metallacycles (eqs. 1.9 - 1.10).[29,30]


Cp2ZrCl2
LiCPh=CPh-CPh=CPhLi
- 2 LiCl
Cp2Zr
Ph
Ph
Ph
Ph

(1.9)

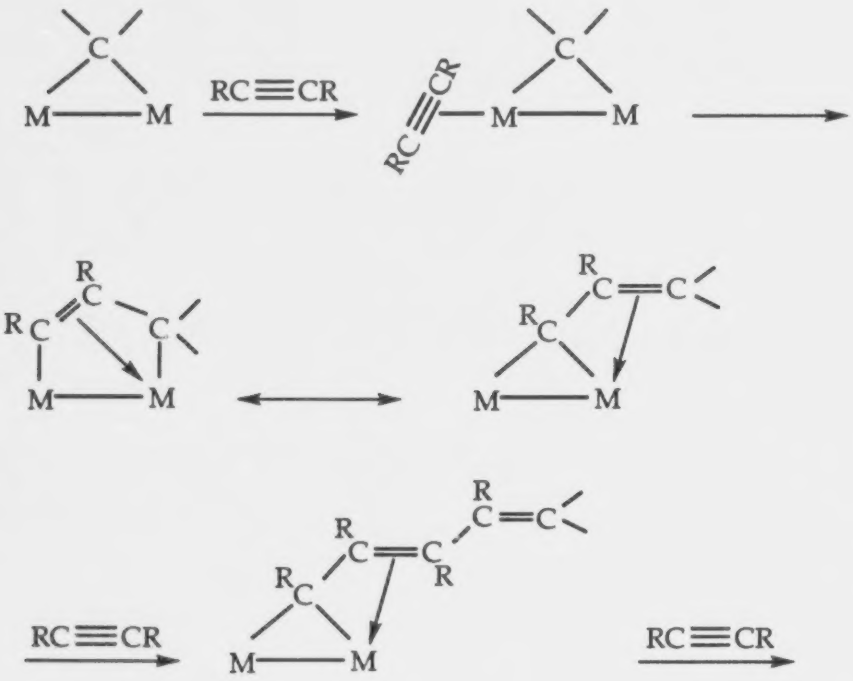

Pt(COD)I2
C6H5(CH2MgCl)2
- 2 MgClI
(COD)Pt

(1.10)

1.1.2 Dinuclear Metallacyclic Complexes

Although most homogeneous catalysts are mononuclear complexes, such as Wilkinson's catalyst for hydrogenation reactions[31] and the rhodium catalyst for the Monsanto Acetic Acid Process,[32] much attention has been directed to study complexes containing more than one metal atom during the recent two and a half decades.[33,34] Such complexes are generally referred to as transition metal clusters; that is, the metal atoms are held together by direct metal-metal bonds.[35] The rapid development of transition metal cluster chemistry was mainly stimulated by the prospects of catalytic applications in heterogeneous catalysis. There are several common features between metal cluster and metal surfaces such as multisite interactions with substrate molecules, which can cooperatively facilitate activation and transformation of the substrates, and the high mobility of substrates or ligands which can promote reactions between molecules bonded to the cluster framework or on metal surfaces.[7,36-42] Muetterties called this similarity the "cluster-surface analogy" and treated metal clusters as a tiny piece of metal with chemisorbed species.[38,39] In heterogeneous catalysis, numerous reactions require a catalyst that contains more than one metal. For instance, an $Fe/K-Al_2O_3$ catalyst is used for ammonia synthesis,[43] Cu-ZnO for methanol synthesis,[44] $Pt/Re-Al_2O_3$ for naphtha-reforming,[45,46] and $Co-Mo-S/Al_2O_3$ for hydrodesulfurization.[47] Although many transition metal clusters also function as homogeneous catalysts and are used in a variety of chemical transformations, such as, hydrogenation of alkenes and alkynes, hydroformylation, water-gas shift reaction, and cyclization reactions of alkynes,[34,48,49] Gladfelter has recently pointed out that it is difficult to map out the mechanisms of these catalytic reactions.[33]

In order to understand catalysis of organic reactions by metal surfaces or metal clusters, it is clearly important to consider dinuclear complexes. Such compounds are excellent candidates for the study of metal-metal interactions and potential cooperative behavior towards substrates. They also form a bridge between mononuclear and multinuclear cluster complexes. Chisholm[50] described the importance of dinuclear complexes as "Anything one can do, two can do, too- and it's more interesting". Indeed, it has been established that dimetallacycles are important intermediates in the Fischer-Tropsch synthesis,[51,52] alkyne polymerization (Scheme 1.1),[53] and organic synthesis.[13,21,54-56]



Scheme 1.1. Proposed Mechanism for Alkyne Polymerization by a Dimetallic Complex

Dimetallacycloalkene complexes are implicated in numerous catalytic reactions of alkynes with carbon monoxide.[55] The various structural types of dimetallacycloalkenes are shown in Figure 1.1. In addition, there are a number of compounds that resemble **B** except that the metal atoms are not bonded directly.[56] These complexes are often referred to as dimetallated olefins and will not be discussed here.

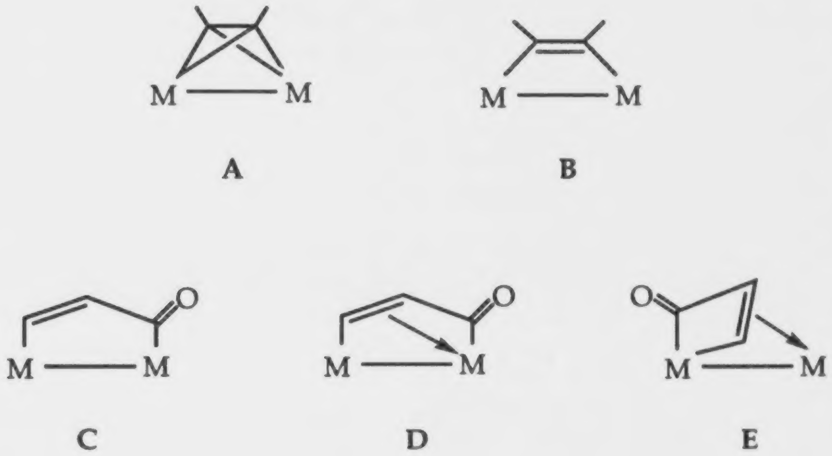
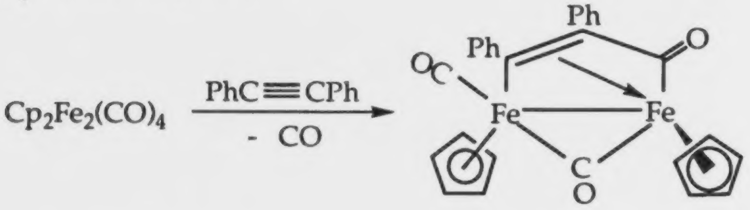


Figure 1.1 Common Types of Dimetallacycloalkenes

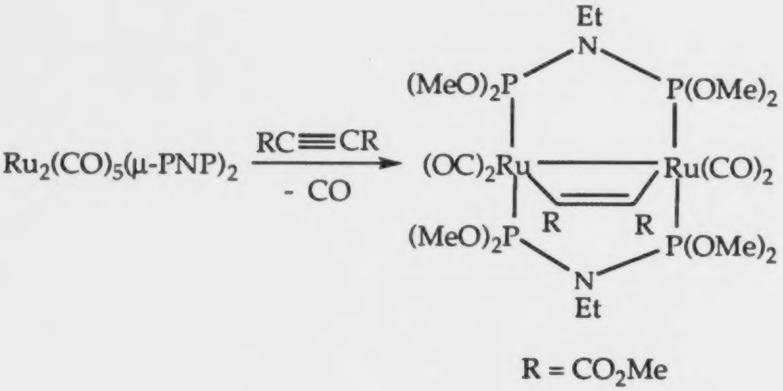
The remarkable structural diversity illustrated in Figure 1.1 is reflected in bonding differences. In structure **A**,[13,57] the alkyne ligand donates four electrons from both of its π-bonds to the two metal atoms. The direction of the C-C bond is therefore perpendicular to the M-M bond,[58] and the complexes are called dimetallatetrahedranes. There are numerous examples of structure type **B** where the alkyne ligand donates two electrons to the metal atoms. The alkyne carbon-carbon bond is oriented parallel to metal-metal bond,[13,57,59-70] and these complexes are called dimetallacyclobutenes. The common feature of structural types of **C**,[65,70-73] **D**,[59,65,74-82] and **E**[83-88] is that the organic ligand contains a α,β-unsaturated ketone moiety, which arises from insertion of a carbonyl into a metal-alkyne carbon bond. The type **D** has been the most common among the structural types of **C**, **D**, and **E**.

Three general synthetic methods have been developed for the preparation of such complexes:

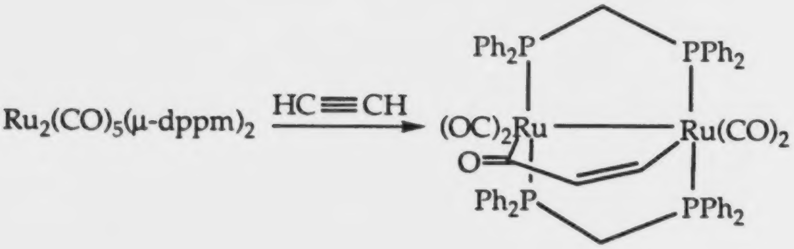
(1) Reaction of dinuclear carbonyl complexes with alkynes (eqs. 1.11 - 1.14):[70,76,89-91]


Cp2Fe2(CO)4
PhC≡CPh
- CO
Ph
Ph
O
OC
Fe
Fe
C
O

(1.11)

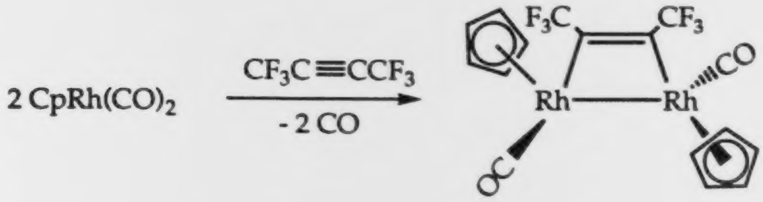

Ru2(CO)5(μ-PNP)2
RC≡CR
- CO
Et
N
(MeO)2P
P(OMe)2
(OC)2Ru
Ru(CO)2
R
R
(MeO)2P
P(OMe)2
N
Et
R = CO2Me

(1.12)


Ru2(CO)5(μ-dppm)2
HC≡CH
Ph2P
PPh2
(OC)2Ru
Ru(CO)2
O
Ph2P
PPh2

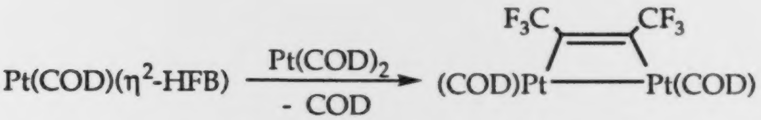
(1.13)

(2) Reaction of mononuclear carbonyl complexes with alkynes:[13]

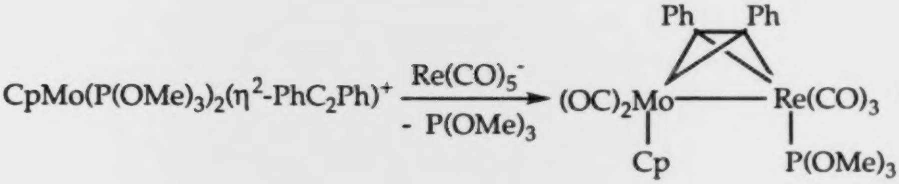

2 CpRh(CO)2
CF3C≡CCF3
- 2 CO
F3C
CF3
CO
Rh
Rh
OC

(1.14)

(3) Condensation reaction of mononuclear alkyne complexes with other transition metal compounds:[92,93]


Pt(COD)(η2-HFB)
Pt(COD)2
- COD
F3C
CF3
(COD)Pt
Pt(COD)

(1.15)


CpMo(P(OMe)3)2(η2-PhC2Ph)+
Re(CO)5-
- P(OMe)3
Ph
Ph
(OC)2Mo
Re(CO)3
Cp
P(OMe)3

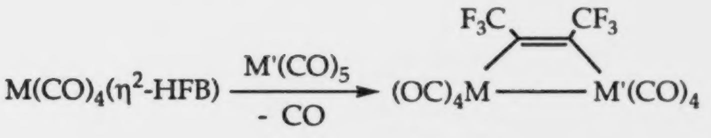
(1.16)

A most common approach to the preparation of dimetallacycloalkenes and dimetallacyclopentenones is the reaction of dinuclear carbonyl complexes with alkynes.[94,95] Many examples have been listed by Hoffman in his comprehensive article.[58] The dinuclear complex precursors either contain a bridging bidentate ligand or do not. The former type of dinuclear complex precursor is more common. The advantage of using bidentate ligands is that they maintain the dinuclear structure during the reaction. Most compounds studied are, however, homobimetallic due to the lack of suitable heterobimetallic precursors. Moreover, these compounds often only react with activated alkynes such as hexafluorobutyne (HFB) and not with electron rich alkynes such as acetylene and 2-butyne which are the typical alkynes involved in organic transformations. An exception to this is the beautiful and extensive work of Knox with $Cp_2M_2(CO)_4$ (M = Fe, Ru), the complexes react with a variety of alkynes yielding a myriad of dimetallacycloalkenes.[53,76,96-98]

The reaction of mononuclear complexes with alkynes often yield a number of alkyne containing complexes. The products are usually separated by careful column chromatography and are thus isolated in low yields. Only in a few cases, purely by chance, did the reaction of mononuclear complexes with alkynes give dimetallacycloalkenes in good yield.[13] Therefore, this method lacks generality.

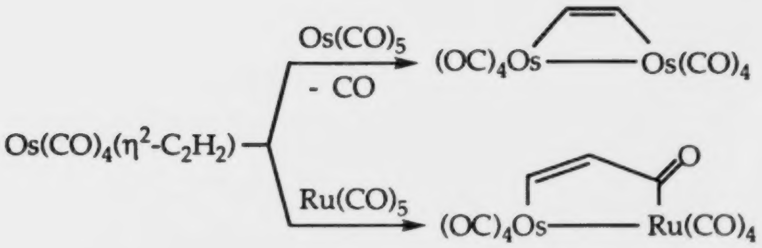
With the above-mentioned complexity in mind, the condensation reaction of mononuclear alkyne complexes with other metal species appears to be a most promising method. Although there are a large number of mononuclear alkyne complexes, prior to our studies, condensation reactions with other transition metal complexes leading to dimetallacycloalkene species had only been briefly studied. Stone[92] had reported that the addition of $Pt(COD)_2$ (COD = cyclo-oct-1,5-diene) with $Pt(COD)(\eta^2\text{-HFB})$ yielded the diplatinum compound $Pt_2(COD)_2(\mu\text{-}\eta^1{:}\eta^1\text{-HFB})$ (eq. 1.15). Later, Beck used a modified approach whereby the addition of an organometallic nucleophiles to a coordinated alkyne on a cationic metal complex afforded dimetallacycloalkenes (eq. 1.16).[93]

The first directed synthesis of dinuclear transition-metal alkyne complexes carried out in our laboratory was by means of the condensation of $M(CO)_4(\eta^2\text{-HFB})$ (M = Ru, Os) with $M'(CO)_5$ (M' = Ru, Os) (eq. 1.17).[66] We found that the 18-electron species, $M(CO)_4(\eta^2\text{-HFB})$, is remarkably reactive towards M'$(CO)_5$, another 18-electron species, to give the corresponding dimetallacyclobutenes. Similar reaction pattern was observed when $(C_5Me_5)M''(CO)_2$ (M" = Co, Rh, Ir) complexes were employed. Since these first observations, the condensation reaction has been extended to a variety of $M(CO)_4(\eta^2\text{-alkyne})$ complexes that have been synthesized and characterized.[59,65,75] A remarkable feature is the ease of reaction between the two 18-electron species. The reactions frequently give surprising results. One of the most interesting findings is the reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with $M(CO)_5$ (M = Ru, Os), as shown in eqs. 1.18a and 1.18b. $Os(CO)_4(\eta^2\text{-}C_2H_2)$ reacts with $Os(CO)_5$ to give the diosmacyclobutene species, which is analogous to those found in eq. 1.17. The reaction with $Ru(CO)_5$, however, leads to the formation of a dimetallacyclopentenone species, which arises from carbonyl insertion into a metal-alkyne bond. As ligand dissociation is normally involved in the reaction of 18-electron complexes, it is very unusual that the reaction of the two 18-electron complexes gives a saturated dimetallacyclopentenone species *without net ligand loss.*



(1.17)

M, M' = Ru, Os



(1.18a)

(1.18b)

1.2 $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) Complexes

Although $M(CO)_5$ (M = Ru, Os) complexes have been known for more than five decades,[99,100] the simple alkyne derivatives, $M(CO)_4(\eta^2\text{-alkyne})$, have not been prepared until a discovery in our laboratory in the late-1980's.[65,66,101] As shown in eq. 1.19, the $M(CO)_4(\eta^2\text{-alkyne})$ complexes are synthesized by photolysis at low temperatures.

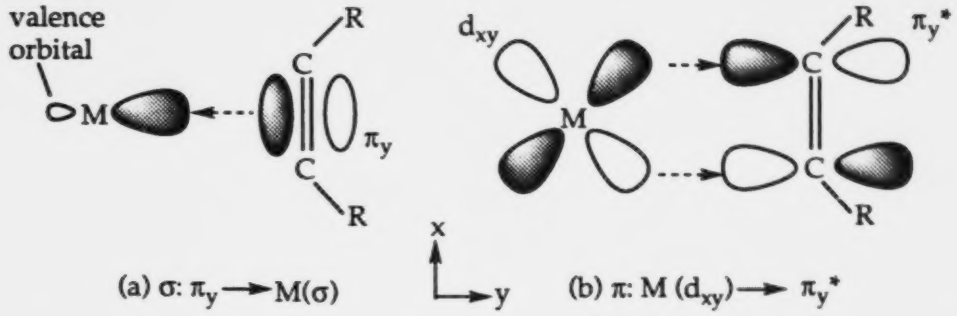
$$M(CO)_5 + RC{\equiv}CR \xrightarrow[\text{L. T., pentane}]{h\upsilon,\ \lambda \geq 370\text{ nm}} M(CO)_4(\eta^2\text{-}RC{\equiv}CR) + CO \qquad (1.19)$$

$M = Ru,\ R = SiMe_3, CF_3;$

$= Os,\ R = SiMe_3, CF_3, H, Me.$

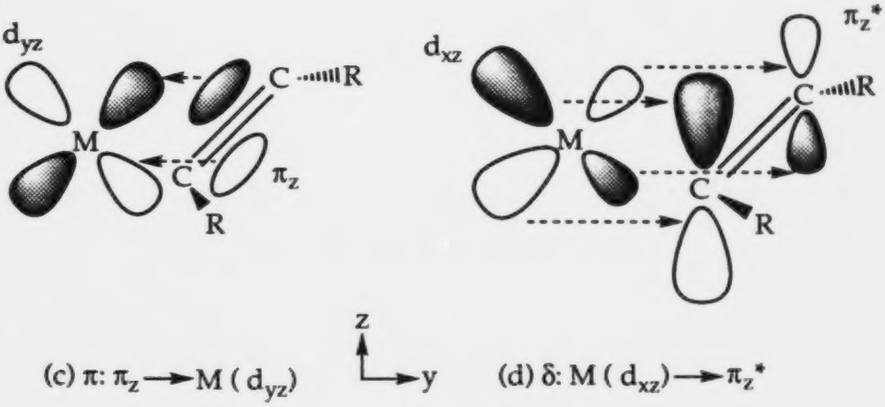
The metal-alkyne bonding is usually described in a similar way as the metal-olefin bonding by Dewar-Chatt-Duncanson model shown in Fig. 1.2.[102-104] The interactions include four components:[32] (a) describes the σ bond formed by donation from the filled alkyne π_y orbital into an empty σ hybrid orbital of the metal; (b) shows the π component derived from back-donation of electron density from the filled metal d_{xy} orbital to the acetylene $\pi_y{}^*$ orbital; (c) illustrates the additional π interaction between the acetylene π_z orbital with the metal d_{yz} orbital; (d) describes the δ component resulting from interaction of the filled d_{xz} orbital with the empty $\pi_z{}^*$ orbital.

In general, the overlap decreases in the order: (a) > (b) > (c) > (d).[105-108] Interactions (a), (b) and (d) are usually bonding. Interaction (c) can be either bonding or antibonding. In early transition metal complexes, donation from the π_z orbital into a low-lying empty d_{yz}



(a) σ: $\pi_y \rightarrow M(\sigma)$

(b) π: M (d_{xy}) → π_y^*



(c) π: $\pi_z \rightarrow M$ (d_{yz})

(d) δ: M (d_{xz}) → π_z^*

Figure 1.2 Bonding in Metal-alkyne Complexes

orbital is important.[109,110] As a result, the alkyne functions as a four-electron donor ligand. For late transition metal complexes in low-oxidation states, the interaction (c) becomes repulsive when the metal d_{yz} orbital is fully occupied and is referred to as four-electron destabilization. Interaction (d) is often neglected because of poor orbital overlap. Therefore, bonding due to interactions (a) and (b) is analogous to the classical metal-olefin bonding. While these synergic interactions are important, the additional interaction (c) of the filled alkyne π_z orbital with a vacant or filled metal d_{yz} orbital further tunes the bonding, it may ultimately influence the chemical behavior of the metal-alkyne complexes and give rise to distinct chemistry.

Whether the alkyne is formally acting as a two-electron or a four-electron donor ligand may be determined by the total electron count of the complex. The vast majority of transition metal carbonyl complexes obey the 18-electron rule; that is, a stable organometallic complex should contain a total of 18 valence electrons.[111] This rule is analogous to the octet rule in organic chemistry. For the transition metal elements, there are five nd, one (n+1)s, and three (n+1)p orbitals. These nine orbitals will mix with the ligand orbitals to form molecular orbitals. The total number of bonding and nonbonding orbitals produced will be nine, independent of the number of the ligands. Thus the rule may be rationalized in terms of filling all nine valence molecular orbitals of the complex by 18 electrons provided by the metal and the ligands. Based on this rule, the alkyne moiety in the $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) complexes is a two-electron donor ligand.

Spectroscopic studies on $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) complexes revealed that they have a trigonal-bipyramidal structure where the alkyne ligand takes up an in-plane equatorial position.[65] This structure has been supported by X-ray crystal structures of $M(CO)_4(\eta^2\text{-}CF_3C_2CF_3)$ (M = Ru, Os) and $Os(CO)_4(\eta^2\text{-}Me_3SiC_2SiMe_3)$.[101,112]

Hoffmann[58,113] has constructed a library of ML_n fragment orbitals, such as $M(CO)_4$ (C_{2v}). As shown in Figure 1.3, the molecular orbital diagram of $M(CO)_4(\eta^2\text{-alkyne})$ complex is constructed by allowing the $M(CO)_4$ (C_{2v}) fragment orbitals to interact with the alkyne orbitals. Before we analyze the interaction of the orbitals and the bonding, it is useful to point out the factors that determine whether a significant bond is formed. These include: (1) the symmetry of the interacting orbitals must be the same, (2) orbital overlap is significant, (3) the energy of the interacting orbitals is similar.[114]

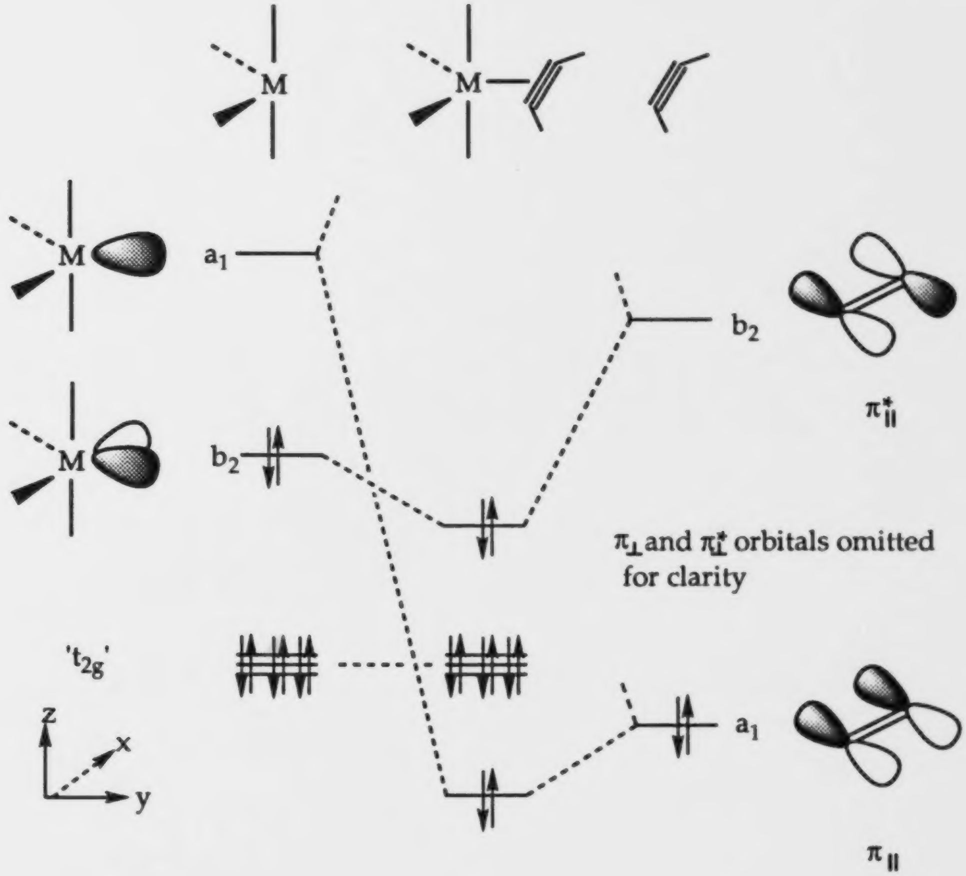

M
M
a_1
b_2
't_{2g}'
z
x
y
b_2
$\pi^*_{\parallel}$
$\pi_{\perp}$ and $\pi^*_{\perp}$ orbitals omitted for clarity
a_1
$\pi_{\parallel}$

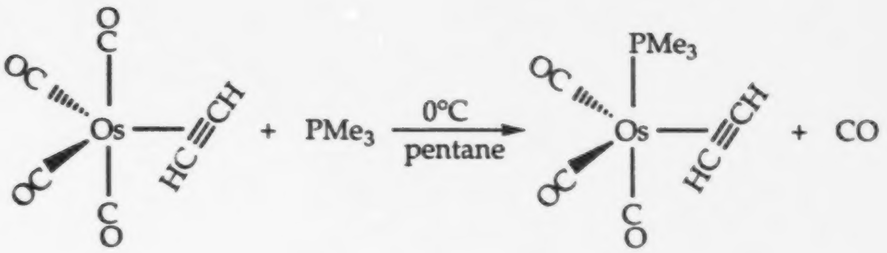
Figure 1.3 Interaction Diagram for $M(CO)_4(\eta^2\text{-alkyne})$

As shown in Fig. 1.3, the interaction between $\pi_{\parallel}$ orbital and the metal a_1 orbital forms the metal-alkyne σ-bond, whereas mixing between the metal b_2 orbital and the alkyne $\pi^*_{\parallel}$ orbital forms the metal-alkyne backbonding interaction. Although the interaction between the alkyne $\pi_{\perp}$ orbital and the metal d_{yz} orbital is not shown in the diagram, it is clear that this is a filled/filled repulsion and has a destabilizing effect. Note that the metal d_{yz} orbital is also responsible for backdonation of metal electron density into the π^* orbitals of the two axial carbonyls.

Another possible orientation of the alkyne ligand is perpendicular to the equatorial plane. Although the σ bond is independent of the rotational orientation of the alkyne, the metal-alkyne backbonding will be significantly different. In this geometry, the backdonation would arise from the unhybridized metal d_{yz} orbital instead of b_2 hybrid that is nicely directed toward the alkyne. However, the metal d_{yz} orbital also interacts with the π^* orbitals of the two axial carbonyls. Furthermore, since the d_{yz} orbital is lower in energy than the b_2 orbital of the $M(CO)_4$ fragment, the backbonding interaction in this case will be poor due to the large separation in energy between the two interacting orbitals. Therefore, the preferred geometry of $M(CO)_4(\eta^2\text{-alkyne})$ is the one that has the alkyne in the equatorial plane.

Reactivity studies carried out in our laboratory show that the carbonyls of $M(CO)_4(\eta^2\text{-alkyne})$ complexes are very labile.[65,66] For example, the carbonyls in $Os(CO)_4(\eta^2\text{-}C_2H_2)$ can be readily exchanged with ^{13}CO at 0°C. In addition, $Os(CO)_4(\eta^2\text{-}C_2H_2)$ reacts with PMe_3 at 0°C to afford the CO substituted product (eq. 1.20).[115]

In contrast, the related 18-electron complexes, $Os(CO)_5$ and $Os(CO)_4(\eta^2\text{-}C_2H_4)$, are inert. Basolo[116] reported that CO substitution in $Os(CO)_5$ occurs at much higher temperatures than observed for $Os(CO)_4(\eta^2\text{-}C_2H_2)$ and the rate of the substitution is considerable only at temperature higher than 96°C. Very recently, Poe[117] reported that the



(1.20)

substitution reaction of the $Os(CO)_4(\eta^2\text{-}C_2H_4)$ complex at 95°C occurs via alkene displacement rather than CO substitution. Therefore, the facile carbonyl replacement in $M(CO)_4(\eta^2\text{-alkyne})$ suggests a direct role of the coordinated alkyne in the reaction (eq. 1.21).

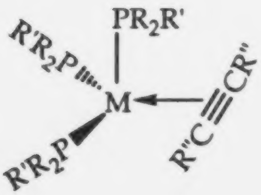
$$Os(CO)_4(\eta^2\text{-alkyne}) \rightleftharpoons Os(CO)_3(\eta^2\text{-alkyne}) + CO \tag{1.21}$$

This marked reactivity change may be rationalized by the weakening of the Os-CO bonds in $Os(CO)_4(\eta^2\text{-alkyne})$ due to the four electron destabilization or by the stabilization of the $Os(CO)_3(\eta^2\text{-alkyne})$ intermediate due to the ability of the alkyne to function as a four electron donor ligand, or a combination of both effects. In order to understand the effect of alkyne on the carbonyl labilization, a structural comparison with the analogous alkene complexes is instructive. Although the molecular structure of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ has not been determined, the structure of the analogous compound $Os(CO)_4(\eta^2\text{-}Me_3SiC_2SiMe_3)$ has been reported.[101]

As shown in Table 1.1, the lengths of the Os-CO (axial) and Os-CO(equatorial) bonds for both compounds are virtually identical. Thus weakening of the Os-CO bonds in the ground state is not obvious. It appears that stabilization of the $Os(CO)_3(\eta^2\text{-alkyne})$ intermediate by the four-electron alkyne ligand is more important. Although the postulated $M(CO)_3(\eta^2\text{-alkyne})$ complexes have so far defied isolation, the isoelectronic compounds $Ir(PMe_2Ph)_3(\eta^2\text{-}C_2Me_2)^+$, $Fe\{P(OMe)_3\}_3(\eta^2\text{-}C_2Ph_2)$, and $Os(CO)(P^iPr_3)_2(\eta^2\text{-}C_2Ph_2)$ are known and have been characterized by X-ray crystallography.[89,112,118] If the coordinated alkyne is a two electron donor ligand, the complexes are sixteen-electron d^8 species and should, therefore, adopt a planar geometry. However, the structure of these molecules has approximate C_s symmetry as shown in Scheme 1.2. The metal-alkyne distances are very short and the C-C bond of the coordinated alkyne has lengthened significantly; on this basis it was argued that the alkyne acts as a four-electron donor.

Table 1.1 Selected Bond Distances for $Os(CO)_4(\eta^2\text{-}C_2H_4)$ and Os $(CO)_4(\eta^2\text{-}C_2(SiMe_3)_2)$

Compound	Bond Distances (Å)	
	Os-CO (ax)	Os-CO (eq)
$Os(CO)_4(\eta^2\text{-}C_2H_4)$[119]	1.943 (17)	1.920 (12)
$Os(CO)_4(\eta^2\text{-}C_2(SiMe_3)_2)$	1.937 (7)	1.925 (8)



M = Ir$^+$, PR_2R' = PMe_2Ph, R" = Me;

= Fe, PR_2R' = $P(OMe)_3$, R" = Ph.

Scheme 1.2: Molecular Structure of $M(PR_3)_3(\eta^2\text{-}C_2R'_2)$

In the case of $Ir(PMe_2Ph)_3(\eta^2\text{-}C_2Me_2)^+$, the orbitals for metal-alkyne interactions have been studied (Figure 1.4).[112] The $d^8\text{-}ML_3$ metal fragment has C_{3v} symmetry. The molecular orbitals are constructed by interacting the set of frontier orbitals of the metal fragment with four alkyne orbitals. The alkyne donates electrons from its $\pi_{\parallel}$ and $\pi_{\perp}$ orbitals to the empty orbitals of the ML_3 fragment, 4a' and 3a', to form the metal-alkyne σ and π bonds. The back donation arises from the filled metal orbitals, 1a" and 2a", to the empty $\pi^*_{\parallel}$ orbital. The interactions $\pi_{\parallel}$ and 1a', and $\pi_{\perp}$ and 2a' are destabilizing, but weak and are compensated by the above mentioned bonding interactions. Thus, three metal-alkyne bonds, including one σ bond, one metal to alkyne π back bond, and one alkyne to metal π bond, are present, which is the so called four-electron donation.[110]

It is well documented that π donation can stabilize the product of ligand dissociation.[110,120-122] For instance, facile CO ligand exchange in the $W(OR)(CO)_5^-$ complex takes place at ambient temperature (1.23).[123]

$$W(OR)(CO)_5^- \underset{+\ CO}{\overset{-\ CO}{\rightleftharpoons}} W(OR)(CO)_4^- \underset{-\ ^{13}CO}{\overset{+\ ^{13}CO}{\rightleftharpoons}} W(OR)(CO)_4(^{13}CO) \qquad (1.23)$$

The rapid incorporation of ^{13}CO is ascribed to the π stabilization of the unsaturated five coordinate intermediate by the alkoxide ligand. While the stabilization of the intermediate by π donation is quite plausible, the filled/filled interactions (four electron destabilization) are also present in the ground state.

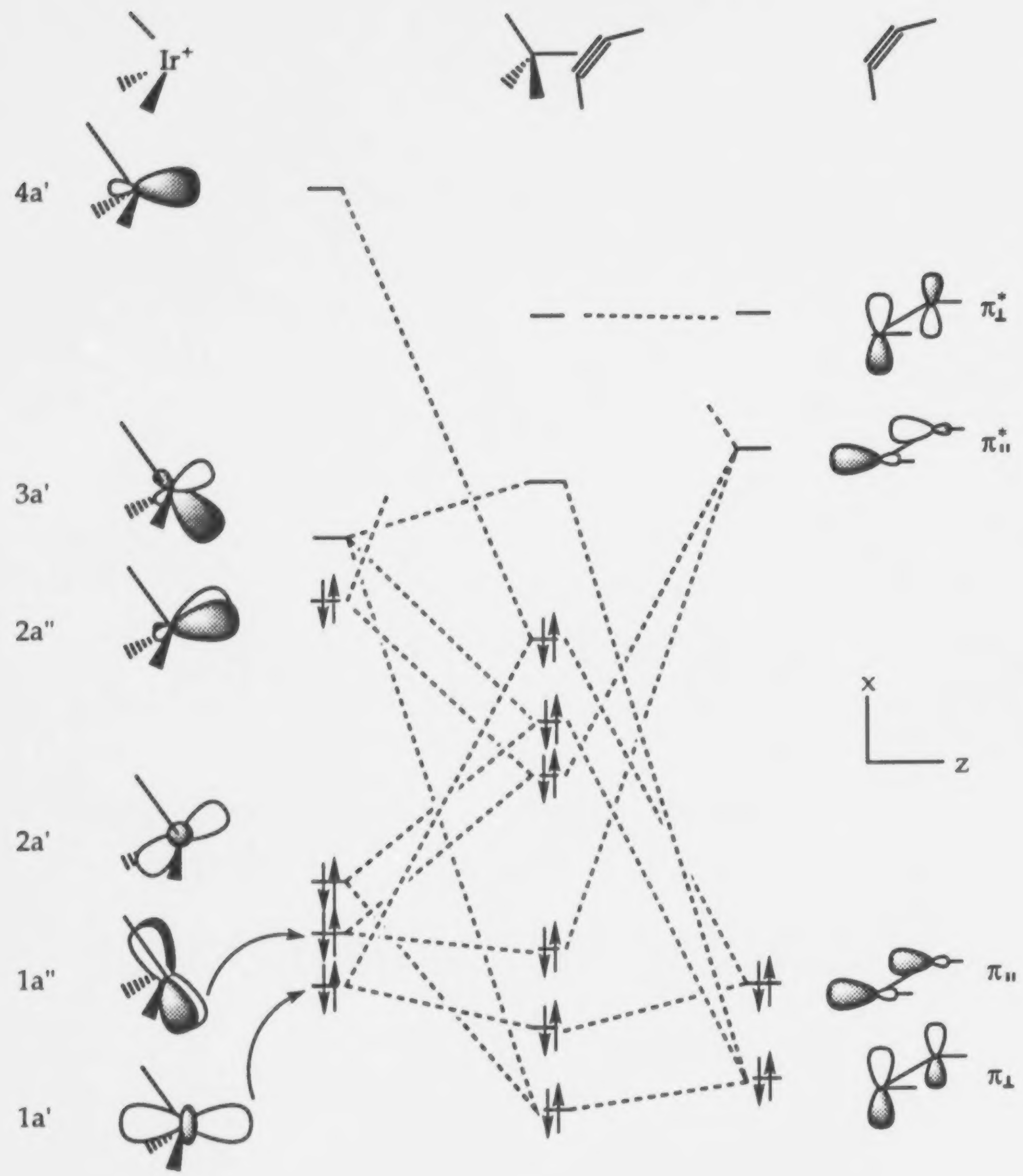

Ir⁺
4a'
3a'
2a"
2a'
1a"
1a'
π⊥*
π∥*
x
z
π∥
π⊥

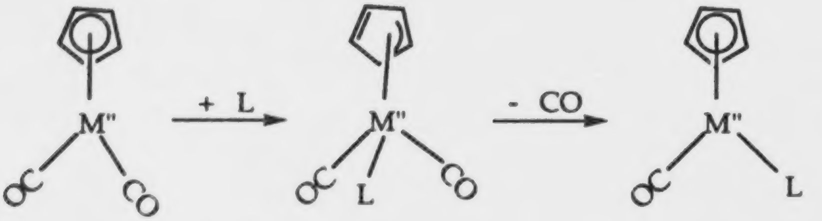
Figure 1.4: Interaction Diagram for $Ir(PMe_2Ph)_3(\eta^2\text{-}C_2Me_2)^+$

1.3 Scope of the Thesis

Previous work established that the condensation reactions of $M(CO)_4(\eta^2\text{-alkyne})$ complexes with other 18-electron compounds, such as $M(CO)_5$ (M= Ru, Os) and $CpM''(CO)_2$ (M" = Co, Rh, Ir), produced a variety of dimetallacyclic products; the nature of the products were found to depend on the metal, alkyne and ancillary ligand.[66,75,101,124] However, attempts to obtain mechanistic information about the reactions by low temperature NMR monitoring were largely unsuccessful. It was hoped that, by carrying out a systematic investigation on the reactivity of $M(CO)_4(\eta^2\text{-alkyne})$ complexes, and on the reactions between them and suitable $M(CO)_4L$ derivatives, further insight into the condensation reactions might be gained.

Before indicating the specifics, it is instructive to highlight the established features of $M(CO)_5$ (M= Ru, Os) and $CpM''(CO)_2$ (M" = Co, Rh, Ir) complexes. Detailed kinetic studies on CO substitution reactions of $M(CO)_5$ (M= Ru, Os) complexes have been reported by Poe and Basolo.[116,125,126] These reactions proceed by a dissociative mechanism requiring either above room temperature conditions or Me_3NO activation at ambient temperatures (1.24). In contrast, the $CpM''(CO)_2$ (M" = Co, Rh, Ir) complexes undergo associative substitution via a ring-slippage process, but again at elevated temperatures (1.25).[127,128]

$$M(CO)_5 \xrightarrow{-\ CO} \text{"}M(CO)_4\text{"} \xrightarrow{+\ L} M(CO)_4L \qquad (1.24)$$



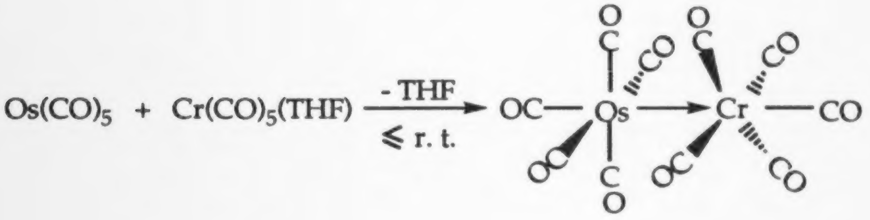
(1.25)

Although there is a fundamental difference between the two mechanisms, a common feature is that these reactions occur at temperatures much higher than the condensation reactions with $M(CO)_4(\eta^2\text{-alkyne})$ complexes. This indicates that CO dissociation from $M(CO)_5$ or $CpM''(CO)_2$ complexes as the initiation step of the condensation reactions is most unlikely because these reactions typically occur at temperatures lower than 0°C.

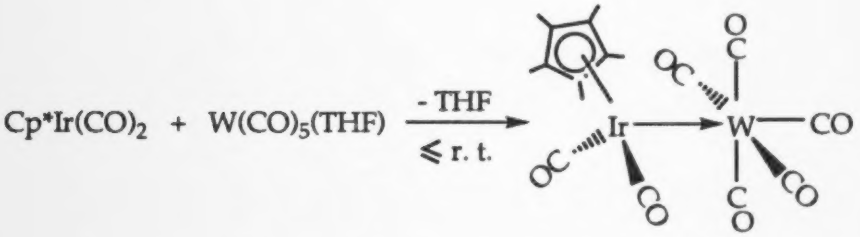
It is generally accepted that electron-rich transition metal complexes can serve as electron donors,[129] and consequently may be used as ligands to other metal centers in the formation of metal-metal bonds. This is an important feature of $M(CO)_5$ and $CpM''(CO)_2$ complexes. For example, the dinuclear complexes $M_2(CO)_9$ (M = Fe, Ru, Os) may be envisaged to form in this fashion (1.26).[130,131]

$$M(CO)_5 \ + \ \text{"}M(CO)_4\text{"} \longrightarrow (OC)_5M \rightarrow M(CO)_4 \longrightarrow M_2(CO)_9 \quad (1.26)$$

More recently, Pomeroy has reported the synthesis of a number of heteronuclear complexes that contain unbridged dative metal-metal bonds.[132-136] As illustrated in eqs. 1.27 and 1.28, the dinuclear complexes $(OC)_5OsCr(CO)_5$ and $(\eta^5\text{-}C_5Me_5)(CO)_2IrW(CO)_5$ were synthesized by displacing a THF ligand from $M'(CO)_5(THF)$ (M' = Cr, W) with the complexes $Os(CO)_5$ and $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$. The dative metal-metal bond is formed by donation of two electrons from the eighteen electron metal center to an empty orbital of the sixteen electron $M'(CO)_5$ fragment. Reactions of this type usually proceed under mild conditions similar to the condensation reactions of $M(CO)_5$ and $CpM''(CO)_2$ complexes with $M(CO)_4(\eta^2\text{-alkyne})$ derivatives. Thus we felt that the nucleophilicity of both $M(CO)_5$ and $CpM''(CO)_2$ complexes, acting as ligands, might play an important role in the condensation reactions with $M(CO)_4(\eta^2\text{-alkyne})$ complexes.



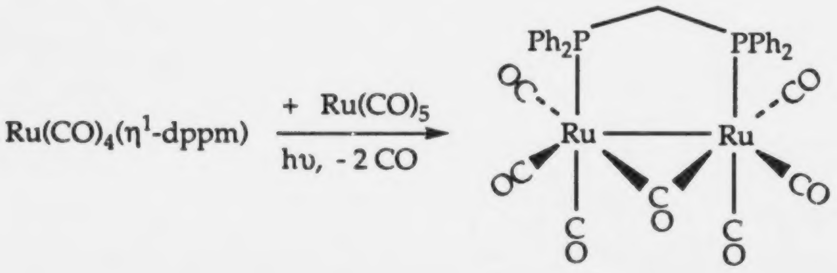
(1.27)



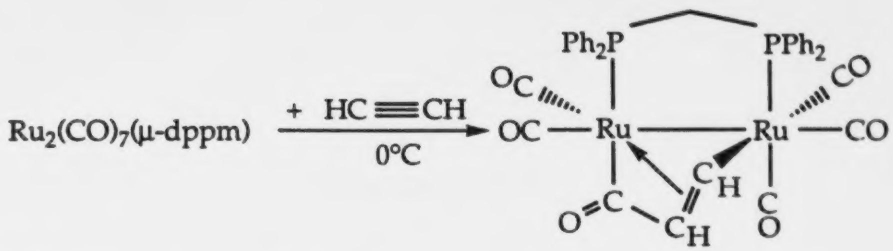
(1.28)

The first objective of this thesis, therefore, was to thoroughly investigate the reaction of $M(CO)_4(\eta^2\text{-alkyne})$ with classical Lewis bases, namely phosphines. It is well known that the properties of phosphines can be changed significantly by changing the substituents.[137] The variations are usually rationalized in terms of electronic and steric effects.[138,139] Based on the results of facile ^{13}CO enrichment of $M(CO)_4(\eta^2\text{-alkyne})$ and the earlier described substitution reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with PMe_3, it was desirable to carry out the reactions of $M(CO)_4(\eta^2\text{-alkyne})$ complexes with a variety of monophosphines (such as PMe_3, PPh_3, P^tBu_3, etc.) to establish whether more than one CO could be substituted or different type of products would form. Next, the reactions of diphosphines with $M(CO)_4(\eta^2$-alkyne) complexes were of interest in hope of obtaining complexes of the type $M(CO)_3(\eta^2$-alkyne)(η^1-dppm). Since bidentate phosphines, such as dppm and dmpm, have been extensively used to bridge two metal centers,[140,141] it was anticipated that these complexes could react with other transition metal complexes, such as $Ru(CO)_4(\eta^2-C_2H_4)$, a source of "$Ru(CO)_4$" fragment,[142,143] to synthesize alkyne containing dinuclear complexes.

Like diphosphines, the complexes $M(CO)_4(\eta^1$-dppm) (M = Fe, Ru) can also be considered as bidentate ligands in which both the 18-electron metal center and the free end of the dppm ligand might coordinate to another metal center to generate dinuclear complexes. Shaw[80,144] reported the use of $Fe(CO)_4(\eta^1$-dppm) complex in the synthesis of a number of heterobimetallic complexes. $Ru(CO)_4(\eta^1$-dppm) has been utilized in our laboratory as a building block in the formation of dinuclear complexes.[74] An example is the preparation of $Ru_2(CO)_7(\mu$-dppm) illustrated in eq. 1.29. Interestingly, this dinuclear complex readily reacts with acetylene to give the dimetallacyclopentenone species (1.30).



(1.29)



(1.30)

Thus it was of interest to investigate the reactions of $M(CO)_4(\eta^1\text{-dppm})$ with $M(CO)_4(\eta^2\text{-alkyne})$ complexes in order to determine if these reactions would yield similar dimetallacyclic complexes. The presence of the alkyne ligand on one metal center and the bridging ligand (dppm) on the other might stabilize reactive intermediates whose analogues were not observed in the condensation reactions of $M(CO)_5$ with $M(CO)_4(\eta^2\text{-alkyne})$ complexes. Furthermore, mechanistic studies on these reactions might provide insight into how carbon-carbon bond formation occurs and how the two metals and the ligands are involved in these processes. Finally, reactivity studies on the obtained complexes were of interest with a view to further study the properties of dimetallacycles.

1.4 References

(1) Lindner, E. *Adv. Heterocycl. Chem.* **1986**, *39*, 237.

(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987, pp 459-520.

(3) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1.

(4) Wilke, G. *Pure Appl. Chem.* **1978**, *50*, 677.

(5) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

(6) Puddephatt, R. J. *Comments Inorg. Chem.* **1982**, *2*, 69.

(7) Ugo, R. *Catal. Rev. Sci. Eng.* **1975**, *11*, 225.

(8) Bergman, R. G. *Pure Appl. Chem.* **1981**, *53*, 161.

(9) Hindermann, J. P.; Hutchings, G. J.; Kiennemann, A. *Catal. Rev. Sci. Eng.* **1993**, *35*, 1.

(10) Bell, A. T. *Catal. Rev. Sci. Eng.* **1981**, *23*, 203.

(11) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

(12) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chew. Rev.* **1983**, *83*, 135.

(13) Dickson, R. S. *Polyhedron* **1991**, *10*, 1995.

(14) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1.

(15) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739.

(16) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272.

(17) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298.

(18) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157.

(19) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979,** *101,* 1123.

(20) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Syntheses via Metal Carbonyls*; I. Wender and P. Pino, Ed.; Wiley-Interscience: New York, 1977; Vol. 2; pp 43-231.

(21) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation. Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991.

(22) Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. (A)* **1970**, 2981.

(23) Herrea, A.; Hoberg, H.; Mynott, R. *J. Organomet. Chem.* **1981,** *222,* 331.

(24) Hoberg, H.; Herrera, A. *Angew. Chem. Int., Ed. Engl.* **1981,** *20,* 876.

(25) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; G. Wilkinson, F. G. A. Stone and E. W. Abel, Ed.; 1982; Vol. 8; pp 499.

(26) Schrock, R. R. *J. Organomet. Chem.* **1986,** *300,* 249.

(27) Schrock, R. R. *Acc. Chem. Res.* **1986,** *19,* 342.

(28) Weinstock, I. A.; Schrock, R. R.; Davies, W. M. *J. Am. Chem. Soc.* **1991,** *113,* 135.

(29) Braye, E. H.; Hubel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961,** *83,* 4406.

(30) Lappert, M. F.; Martin, T. R. *J. Chem. Soc., Chem. Comm.* **1980,** 476.

(31) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987, pp 530-535.

(32) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Wadsworth, Inc.: Belmont, CA., 1985, pp 388-410.

(33) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; D. F. Shriver, H. D. Kaesz and R. D. Adams, Ed.; VCH Publishers: New York, 1990; pp 329.

(34) Suss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993,** *35*, 41.

(35) Cotton, F. A. *Quart. Rev., Chem. Soc.* **1966,** *20*, 389.

(36) Chini, P. *Inorg. Chim. Acta. Rev.* **1968,** 2, 31.

(37) Lewis, J.; Johnson, B. F. G. *Pure Appl. Chem.* **1975,** *44*, 43.

(38) Muetterties, E. L. *Science* **1977,** *196*, 839.

(39) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979,** *79*, 91.

(40) Muetterties, E. L. *Chem. Soc. Rev.* **1982,** *11*, 283.

(41) Hoffmann, R. J. *J. Phys., Condens. Matter* **1993,** *5*, A1.

(42) Canning, N. D. S.; Madix, R. J. *J. Phys. Chem.* **1984,** *88*, 2437.

(43) Boudart, M. *Catal. Rev. Sci. Eng.* **1981,** *23*, 1.

(44) Cybulski, A. *Catal. Rev. Sci. Eng.* **1994,** *36*, 557.

(45) Ciapetta, F. G.; Wallace, D. N. *Catal. Rev.* **1971,** *5*, 67.

(46) Biswas, J.; Bickle, G. M.; Gray, P. G.; Do, D. D.; Barbier, J. *Catal. Rev. Sci. Eng.* **1988,** *30*, 161.

(47) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev. Sci. Eng.* **1989,** *31*, 1.

(48) Muetterties, E. L.; Krause, H. J. *Angew, Chem. Int. Ed. Engl.* **1983,** *22*, 135.

(49) Gates, B. C. In *Metal Clusters in Catalysis*; B. C. Gates, L. Guczi and H. Knozinger, Ed.; Elsevier: Amsterdam, The Netherlands, 1986; pp 497.

(50) Chisholm, M. H. In *Reactivity of Metal-Metal Bonds* ; ACS Symp. Ser.: 1981; Vol. 155; pp 17-39.

(51) Brady, R. C.; Pettit, R. *J Am. Chem. Soc.* 1980, *102*, 6181.

(52) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1981,** *103,* 1287.

(53) Dyke, A. F.; Finnimore, S. R.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Riding, G. H.; Taylor, G. E. In *Reactivity of Metal-Metal Bonds;* ACS Symp. Ser.: 1981; Vol. 155; pp 259-271.

(54) Schore, N. E. *Chem. Rev.* **1988,** *88,* 1081.

(55) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis;* John Wiley & Sons: New York, 1992, pp 191-216.

(56) Adams, R. D. *Chem. Soc. Rev.* **1994,** 335.

(57) Acum, G. A.; Mays, M. J.; Raithby, P. R.; Solan, G. A. *J. Chem. Soc., Dalton Trans.* **1995,** 3049.

(58) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982,** *104,* 3858.

(59) Takats, J. *J. Cluster Sci.* **1992,** *3,* 479.

(60) Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990,** *29,* 508.

(61) Cotton, F. A.; Feng, X. *Inorg. Chem.* **1990,** *29,* 3187.

(62) Calhorda, M. J.; Hoffmann, R. *Organometallics* **1986,** *5,* 2181.

(63) Adams, R. D.; Daran, J. C.; Yeannin, Y. *J. Cluster Sci.* **1992,** *3,* 1.

(64) Burke, M. R.; Seils, F.; Takats , J. *Organometallics* **1994,** *13,* 1445.

(65) Burn, M. J.; Kiel, G.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989,** *111,* 6850.

(66) Gagne, M. R.; Takats, J. *Organometallics* **1988,** *7,* 561.

(67) Takats, J. *Polyhedron* **1988,** *7,* 931.

(68) Field, J. S.; Haines, R. J.; Sundermeyer, J.; Woollam, S. F. *J. Chem. Soc., Dalton Trans.* **1993,** 3749.

(69) Sutherland, B. R.; Cowie, M. *Organometallics* **1984,** *3,* 1869.

(70) Mirza, M. A.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1994,** *13,* 3063.

(71) Dickson, R. S.; Gatehouse, B. M.; Nesbit, M. C.; Pain, G. N. *J. Organomet. Chem.* **1981,** *215*, 97.

(72) Johnson, K. A.; L., G. W. *J. Am. Chem. Soc.* **1991,** *113*, 5097.

(73) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1992,** *11*, 2534.

(74) Kiel, G.; Takats, J. *Organometallics* **1989,** *8*, 839.

(75) Takats, J.; Washington, J.; Santarsiero, B. *Organometallics* **1994,** *13*, 1078.

(76) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

(77) Hogarth, G.; Knox, S. A. R.; Lloyd, B. R.; Macpherson, K. A.; Morton, D. A. V.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 360.

(78) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1988**, 358.

(79) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1987**, 662.

(80) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 741.

(81) Wong, A.; Pawlick, R. V.; Thomas, C. G.; Leon, D. R.; Liu, L. *Organometallics* **1991,** *10*, 530.

(82) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Parisini, E.; Martinelli, M.; Gallop, M. A.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1992,** 807.

(83) Azar, M.; Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *J. Am. Chem. Soc.* **1985,** *107*, 7209.

(84) Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987,** *6*, 2298.

(85) Chetcuti, M. J.; Green, K. A. *Organometallics* **1988,** *7*, 2450.

(86) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *J. Am. Chem. Soc.* **1989,** *111*, 2743.

(87) Finnimore, S. R.; Knox, A. A. R.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980,** 411.

(88) Dickson, R. S.; Evans, G. S.; Fallon, G. D. *Aust. J. Chem.* **1985,** *38*, 273.

(89) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Oro, L. A. *J. Organomet. Chem.* **1994,** *468*, 223.

(90) Jenkins, J. A.; Cowie, M. *Organometallics* **1992,** *11*, 2774.

(91) Wang, L. S.; Cowie, M. *Can. J. Chem.* **1995,** *73*, 1058.

(92) Boag, N. M.; Green, M.; Stone, F. G. *J. Chem. Soc., Chem. Commun.* **1980,** 1281.

(93) Beck, W.; Muller, H.; Nagel, V. *Angew. Chem., Int. Ed. Engl.* **1986,** *25*, 734.

(94) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983,** *83*, 203.

(95) Winter, M. J. *Adv. Organomet. Chem.* **1989,** *29*, 101.

(96) Knox, S. A. R. *Pure & Appl. Chem.* **1984,** *56*, 81.

(97) Gracey, B. P.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1985,** 1935.

(98) Knox, S. A. R. *J. Organomet. Chem.* **1990,** *400*, 255.

(99) Manchot, W.; Manchot, W. J. *Z. Anorg. Allg. Chem.* **1936,** *226*, 385.

(100) Heiber, W.; Stallmann, H. *Z. Elektrochem.* **1943,** *49*, 288.

(101) Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* **1987,** *6*, 1918.

(102) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951,** *18*, C71.

(103) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953,** 2939.

(104) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979,** *101*, 783.

(105) Nelson, J. H.; Wheelock, K. S.; Cusachs, L. C.; Jonassen, H. B. *J. Am. Chem. Soc.* **1969,** *91*, 7005.

(106) Nelson, J. H.; Jonassen, H. B. *Coord. Chem. Rev.* **1971**, *6*, 27.

(107) Nelson, J. H.; Wheelock, K. S.; Cusachs, L. C.; Jonassen, H. B. *Inorg. Chem.* **1972**, *11*, 422.

(108) Wheelock, K. S.; Nelson, J. H.; Cusachs, L. C.; Jonassen, H. B. *J. Am. Chem. Soc.* **1970**, *92*, 5110.

(109) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466.

(110) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

(111) Elschenbroich, C.; Salzer, A. *Organometallics-A Concise Introduction;* 2nd ed.; VCH Publishers: New York, 1992, pp 186.

(112) Marinell, G.; Streib, W. E.; Huffman, J. C.; Caulton, K. G.; Gagne, M. R.; Takats, J.; Dartiguenave, M.; Chardon, C.; Jackson, S. A.; Eisenstein, O. *Polyhedron* **1990**, *9*, 1867.

(113) Hoffmann, R. *Science* **1981**, *211*, 995.

(114) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(115) Kiel, G.; Takats, J., Unpublished work.

(116) Shen, J.; Gao, Y.; Shi, Q.; Basolo, F. *Organometallics* **1989**, *8*, 2144.

(117) Huber, B. J.; Poe, A. J. *Inorg. Chim. Acta* **1994**, *227*, 215.

(118) Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

(119) Bender, B. R.; Norton, J. R.; Miller, M. M.; Anderson, O. P.; Rappe, A. K. *Organometallics* **1992**, *11*, 3427.

(120) Tobe, M. L. *Acc. Chem. Res.* **1970**, *3*, 377.

(121) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

(122) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

(123) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H. *Inorg. Chem.* **1988**, *27*, 3269.

(124) Washington, J. Ph. D. Thesis, University of Alberta, 1994.

(125) Huq, R.; Poe, A. J.; Chawla, S. *Inorg. Chim. Acta* **1980**, *38*, 121.

(126) Shen, J.; Gao, Y.; Shi, Q.; Basolo, F. *Inorg. Chem.* **1989**, *28*, 4304.

(127) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657.

(128) Vest, P.; Anhaus, J.; Bajai, H. C.; Eldik, R. V. *Organometallics* **1991**, *10*, 818.

(129) Shriver, D. F. *Acc. Chem. Res.* **1970**, 231.

(130) King, R. B. *Organomet. Syn.* **1965**, *1*, 93.

(131) Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95.

(132) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854.

(133) Einstein, F. W. B.; Jones, T.; Pomeroy, R. K.; Rushman, P. *J. Am. Chem. Soc.* **1984**, *106*, 2707.

(134) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *4*, 250.

(135) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K. *Organometallics* **1989**, *8*, 1030.

(136) Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K.; Shipley, J. A. *Inorg. Chem.* **1992**, *31*, 3155.

(137) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(138) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

(139) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

(140) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.

(141) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(142) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Organomet. Chem.* **1974**, *67*, C75.

(143) Linder, E. L.; Jansen, R.; Mayer, H. A.; Hiller, W.; Fawzi, R. *Organometallics* **1989**, *8*, 2355.

(144) Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans*. **1987**, 2751.

Chapter 2

Reactions of $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) with Monophosphines

Introduction

The reactions of transition metal complexes with alkynes have been extensively studied due to their practical importance in organic synthesis.[1-4] However, in many cases, the reactions led to the formation of complex mixtures. For example, the reactions of alkynes with iron carbonyl complexes, investigated mainly by Hübel, yielded a number of organic compounds, such as cyclopentadienones and quinones.[5-7] The intimate mechanisms of these processes, however, are not fully understood. It has been proposed that alkyne activation, by coordination to a transition metal, is a common first intermediate.[7] It is therefore of interest to investigate the synthesis and reactivity of mononuclear metal-alkyne complexes.

Alkyne complexes containing molybdenum and tungsten have been extensively studied by Templeton[8-11], Alt,[12,13] and Davidson.[14,15] Examples of mononuclear alkyne complexes of group VIII and IX transition metals are, however, rather limited. Brintzinger has observed $CpCo(CO)(\eta^2\text{-}C_2Ph_2)$ by IR spectroscopy,[16] but the compound has not been isolated. Prior to our work, there was only one example of a ternary iron-carbonyl alkyne complex, $Fe(CO)_4\{\eta^2\text{-}C_2(SiMe_3)_2\}$.[17]

Interest in our research group led to the synthesis of $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) complexes.[18-20] The key to the successful synthesis of these complexes resided in is the use of low temperature photolysis. As mentioned in Chapter 1, the complexes were found to undergo ready CO exchange and novel condensation reactions with other 18-electron species ($M(CO)_5$ and $Cp'M'(CO)_2$, M' = Co, Rh, Ir). The mechanisms of the condensation reactions, however, remained elusive. As part of our reactivity studies on $M(CO)_4(\eta^2\text{-}RC_2R')$ (M = Ru, R = R' = CF_3. M = Os; R = R' = CF_3; R = CF_3, R' = H; R = R' = H; R = R' = CH_3) complexes with nucleophiles, it was of interest to investigate the reactivity of these species towards classical Lewis bases. The results of the reactivity with monophosphines are presented in this chapter.

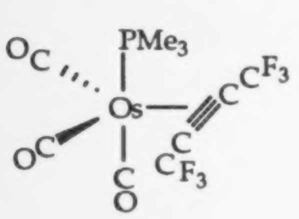
2.2. Results and Discussion

2.2.1. Reactions of $M(CO)_4(\eta^2\text{-}RC_2R')$ (M = Ru, R = R' = CF_3; M = Os, R = R' =CF_3; R = H, R' = CF_3) with PR''_3 (R" = CH_3, Ph)

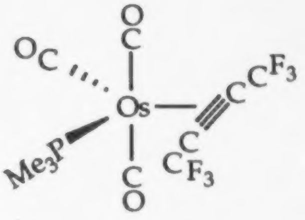
Initial studies focussed on the thermally stable hexafluorobutyne and trifluoropropyne derivatives. Reaction of $Os(CO)_4(\eta^2\text{-HFB})$ (**1a**) with one equivalent of PMe_3 proceeded readily and gave the monosubstituted product **2a** (eq. 2.1). The reaction was monitored by IR spectroscopy. Another minor species **3a**, which will be described later, was also formed. The formulation of the compound is based on elemental analysis and mass spectroscopy.

$$\underset{\textbf{1a}}{Os(CO)_4(\eta^2\text{-}F_3CC_2CF_3)} \xrightarrow[0°C,\ pentane]{+\ PMe_3,\ -CO} \underset{\textbf{2a}}{Os(CO)_3(PMe_3)(F_3CC_2CF_3)} \quad (2.1)$$

As shown below phosphine substitution could give rise to two distinct geometrical isomers **A** or **B**.



A



B

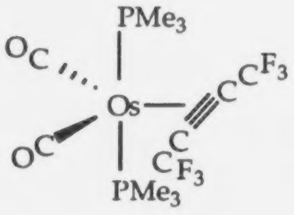
The ^{19}F NMR of **2a** showed one resonance as a doublet at δ - 57.0 ($^4J_{PF}$ = 2.0 Hz), suggesting that compound **2a** has structure **A** as structure **B** would lead to two inequivalent fluorine resonances. The corresponding $^{31}P\{^1H\}$ NMR spectrum exhibited a septet at δ - 43.5 ($^4J_{PF}$ = 2.0 Hz) consistent with the structure **A**. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum, showed a doublet at δ 179.2 ($^2J_{PC}$ = 10.6 Hz) and a doublet at δ 170.4 ($^2J_{PC}$ = 113.0 Hz), with an intensity ratio of 2:1, indicating that two of the carbonyls are equivalent while the third is distinct. In addition, the resonance with the intensity one at δ 170.4 shows a large ^{13}C-^{31}P coupling constant as expected for the *trans* orientation between the phosphine and the carbonyl. Therefore , the NMR spectroscopic data clearly establish the structure of **2a** as having the PMe_3 ligand located in the axial position, i.e. structure **A**.

To investigate the possibility for multisubstitution, the reaction of $Os(CO)_4(\eta^2\text{-HFB})$ with two equivalents of PMe_3 and excess of PMe_3 were carried out. In both cases, the reaction gave the same disubstituted product **3a** (eq. 2.2).

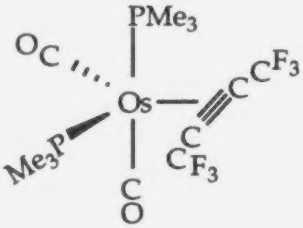
$$\mathrm{Os(CO)_4(\eta^2\text{-}F_3CC_2CF_3)} \xrightarrow[0^\circ\mathrm{C,\ pentane}]{+\ 2\,\mathrm{PMe_3},\ -\ 2\,\mathrm{CO}} \mathrm{Os(CO)_2(PMe_3)_2(F_3CC_2CF_3)} \quad (2.2)$$

3a

The formulation of compound **3a** is based on mass spectrometry and elemental analysis. The molecular ion and sequential loss of two carbonyls were observed in the mass spectrum. On the basis of the geometry of the monosubstituted product **2a**, the two most likely structures are shown below.



C



D

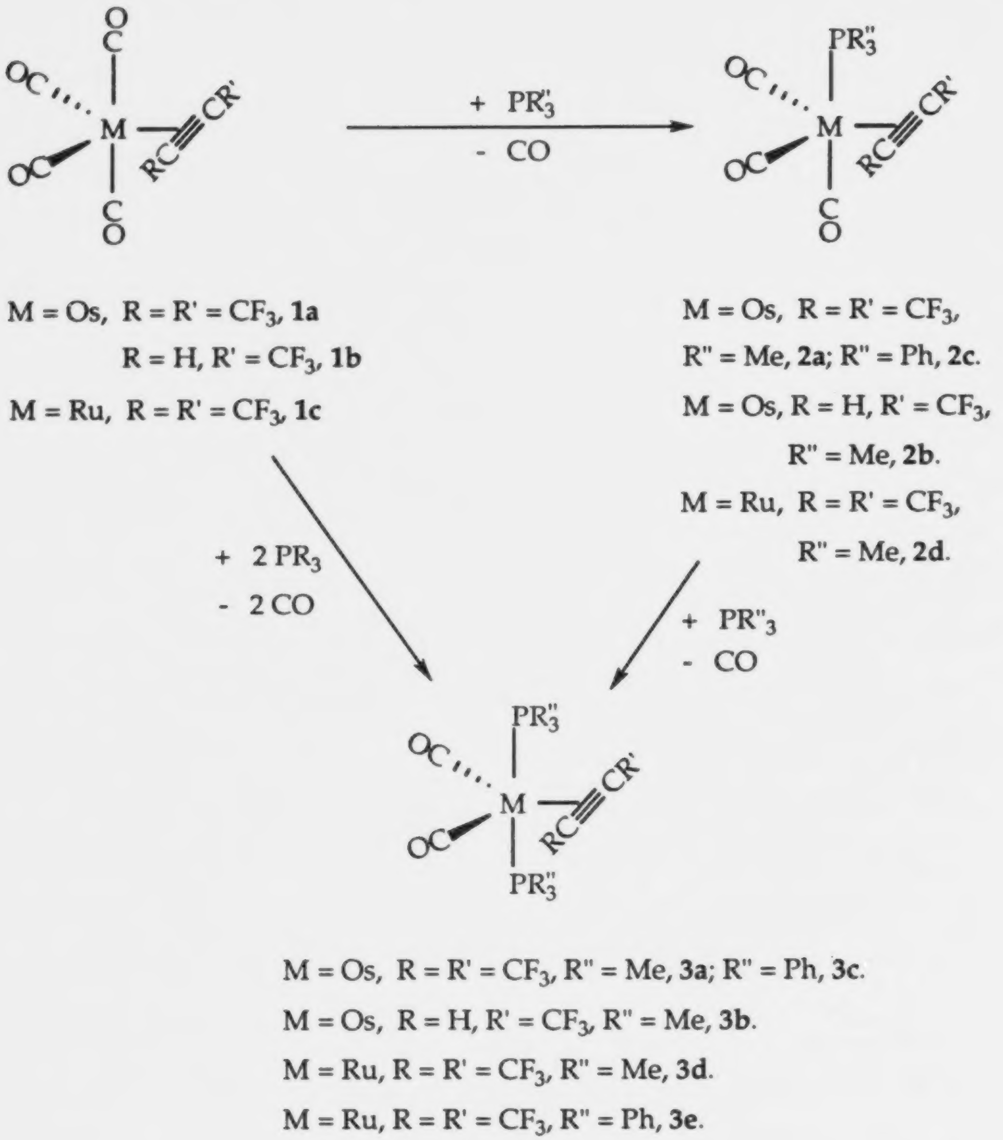
The $^{31}P\{^1H\}$ NMR spectrum of **3a** showed a single resonance as a septet at δ - 42.7 ($^4J_{PF}$ = 3.06 Hz) suggesting structure **C** with equivalent phosphines. The presence of only one ^{19}F NMR signal as a triplet at δ - 55.2 ($^4J_{PF}$ = 3.06 Hz) is also in accord with structure **C**. Moreover, the observations of a single $^{13}C\{^1H\}$ NMR signal in the carbonyl region as a triplet at δ 186.0 ($^2J_{PC}$ = 7.8 Hz) and one ^1H NMR signal as a pseudotriplet at δ1.42 (J_{PH} = 3.8 Hz) provide further support for structure **C**. The appearance of the ^1H NMR signals as a pseudotriplet is attributed to virtual coupling.[21,22] Thus, all NMR spectroscopic data are in accord with structure **C**.

Reaction of the trifluoropropyne derivative, $Os(CO)_4(\eta^2\text{-}F_3CC_2H)$ (**1b**) with PMe_3 proceeded in a similar fashion producing the respective mono- and disubstituted complexes **2b** and **3b**. The only difference is that the reaction of **1b** with one equivalent PMe_3 yielded **2b** cleanly. The spectroscopic parameters are similar to those of **2a** and **3a**, indicating analogous structures (Scheme 2.1).

In contrast to the PMe_3 reactions described above, the reaction of $Os(CO)_4(\eta^2\text{-HFB})$ with one equivalent PPh_3 unexpectedly gave a mixture of two species **2c** and **3c**. Attempts to separate the two compounds were unsuccessful. Pure disubstituted product **3c** was obtained by treating **1c** with two equivalent of PPh_3. This allowed the identification of the spectroscopic signatures of **2c** and **3c** which again are similar to previous substitution products and accordingly are assigned similar structures (Scheme 2.1).

Like the PPh_3 reaction described above, the reaction of $Ru(CO)_4(\eta^2\text{-HFB})$ (**1c**) with one equivalent PMe_3 gave primarily the disubstituted species **3d**, with a very small amounts of monosubstituted product **2d** and unreacted starting material, suggesting that the rate of the second substitution is much faster than that of the first. When the reaction of was carried out with either two equivalents or an excess of PR_3 (R = Me, **3d**; Ph, **3e**) pure disubstituted products **3d** and **3e**, were obtained respectively (Scheme 2.1).

To gain some insight into the steps leading to the formation of mixtures **2c**/**3c** and **2d**/**3d**, the reaction of $Os(CO)_4(\eta^2\text{-HFB})$ with PPh_3 and that of $Ru(CO)_4(\eta^2\text{-HFB})$ with PMe_3 were monitored by low temperature ^1H, ^{31}P, and ^{19}F NMR spectroscopy. Since both reactions share common features, only the former one will be discussed.



M = Os, R = R' = CF_3, **1a**
R = H, R' = CF_3, **1b**
M = Ru, R = R' = CF_3, **1c**

M = Os, R = R' = CF_3,
R'' = Me, **2a**; R'' = Ph, **2c**.
M = Os, R = H, R' = CF_3,
R'' = Me, **2b**.
M = Ru, R = R' = CF_3,
R'' = Me, **2d**.

M = Os, R = R' = CF_3, R'' = Me, **3a**; R'' = Ph, **3c**.
M = Os, R = H, R' = CF_3, R'' = Me, **3b**.
M = Ru, R = R' = CF_3, R'' = Me, **3d**.
M = Ru, R = R' = CF_3, R'' = Ph, **3e**.

Scheme 2.1

Figure 2.1 shows the ^{19}F NMR spectra obtained at different times and temperature during the reaction of $Os(CO)_4(\eta^2\text{-HFB})$ (**1a**) with one equivalent PPh_3. At - 20°C only one ^{19}F NMR signal is observed due to the starting material, $Os(CO)_4(\eta^2\text{-HFB})$. The solution was then allowed to

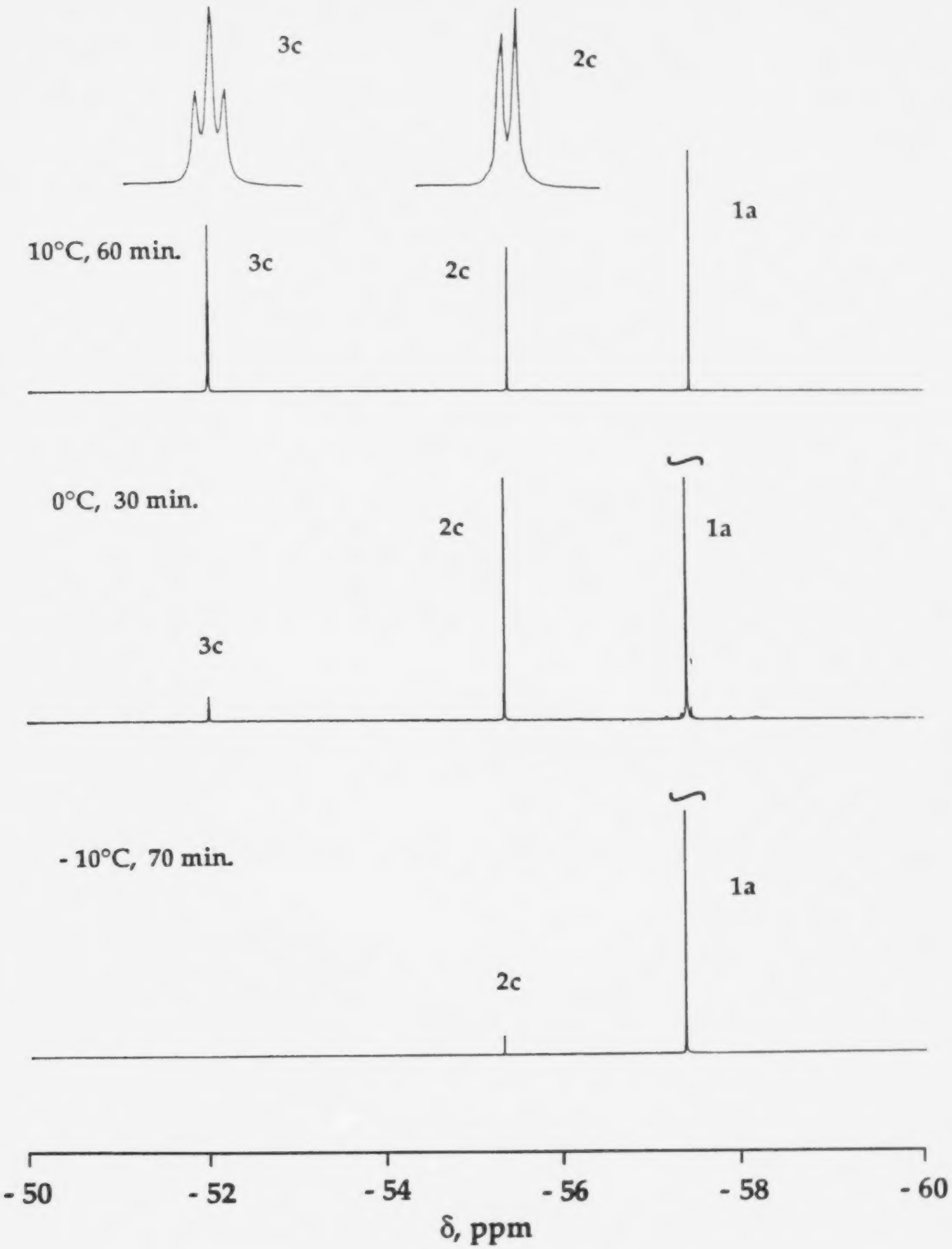


Figure 2.1: Variable Temperature ^{19}F NMR Spectra

warm. At - 10°C, the monosubstituted species **2c** was also seen as a doublet at δ - 55.4 ($^4J_{FP}$ = 1.9 Hz). Further warming to 0°C and maintaining the solution at this temperature for 30 min resulted in the appearance of the new species **3c**. The relative intensity between **2c** and **3c** was 7:1. The intensity ratio gradually decreased to 1:2 when the NMR sample was maintained at + 10°C for 60 minutes. No other peaks were observed. These observations clearly show that the disubstituted product **3c** is formed via the monosubstituted species **2c** as an intermediate. In addition, these observations indicate that the rate of the second substitution is faster than that of the first, and this has been confirmed by a recent kinetic study by Dr. Jean Pearson of our laboratory.[23]

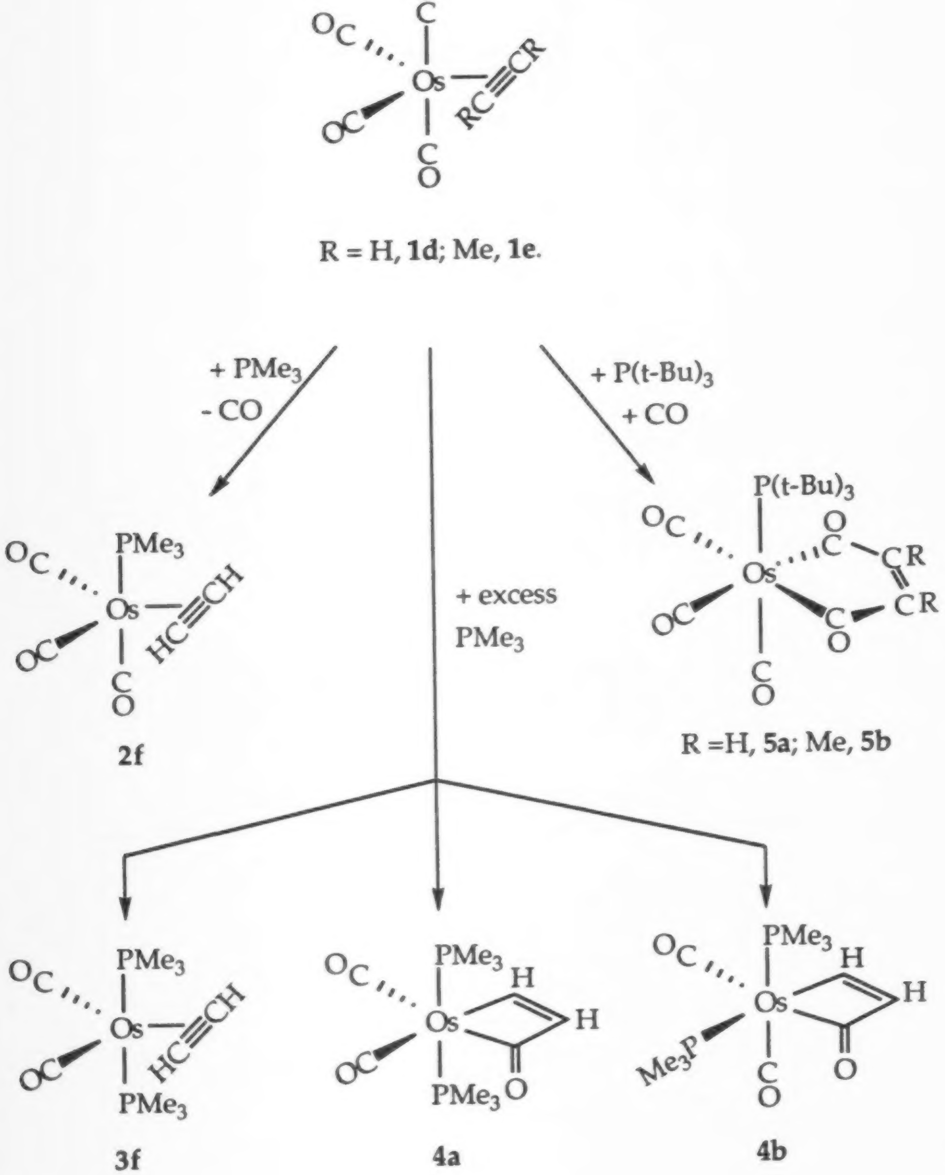
It is well documented that the majority of eighteen electron complexes react by dissociation of a two-electron ligand leading to a high energy, reactive sixteen electron active intermediate. Exceptions to this occur with ligands which exhibit different bonding modes and hapticity, such as, NO and C_5H_5 ligands, and thereby allow for associative substitution.[24-26] Based on this premise, it is likely that CO dissociation from a $M(CO)_4(\eta^2\text{-}RC_2R')$ complex is the rate-determining step. This assumption was corroborated by kinetic studies on the reaction of $Os(CO)_4(\eta^2\text{-HFB})$ with a series of monophosphines,[23] which showed that the rate of the first carbonyl substitution is independent of the nature of the phosphine.

The effect of phosphines on the rate of substitution reactions in octahedral complexes is a well known phenomenon,[26-29] and usually results in CO labilization towards substitution. The origin for such labilization is ascribed to the stabilization of the unsaturated intermediate by the electron-donating phosphine ligand. Indeed, in the case of the reaction of $Os(CO)_4(\eta^2\text{-HFB})$ with PPh_3, the second carbonyl substitution is faster than the first, in line with phosphine labilization arguments. In contrast, with PMe_3 the substitution of the second carbonyl is slower. Thus ground state effects may also play a role as a phosphine ligand would increase the electron density on the metal center thereby enhancing the metal-to-CO backbonding and preventing further CO dissociation. In addition, the kinetic studies showed that the size of the phosphine ligands also influence the rate of the second CO substitution.[23] With a view to understand the role and importance of all these factors, further kinetic studies in our laboratories[30] and theoretical calculations on structures and energy changes of these systems by Prof. M. Klobukowski of this department are underway.

2.2.2. Reactions of $Os(CO)_4(\eta^2\text{-}C_2R_2)$ (R = H, CH_3) with PR'_3 (R' = CH_3, t-C_4H_9)

To establish whether the alkyne had an effect on the substitution, the reactions of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with PMe_3 and $P(^tBu)_3$ were carried out. An earlier study showed that $Os(CO)_3(PMe_3)(\eta^2\text{-}C_2H_2)$ (**2f**) is readily obtained when $Os(CO)_4(\eta^2\text{-}C_2H_2)$ is reacted with one equivalent of PMe_3.[31] Hence the focus here was on the reaction with an excess of PMe_3. Three products **3f**, **4a**, and **4b** were isolated from this reaction in 32%, 26% and 14% yields respectively.

The mass spectrum and elemental analysis of **3f** agreed with the formulation $Os(CO)_2(PMe_3)_2(C_2H_2)$. The molecular ion and the successive loss of two carbonyl groups were observed in the mass spectrum. The IR, ^1H, ^{31}P, and ^{13}C NMR spectroscopic parameters are similar to those of other disubstituted compounds described in the previous section, indicating that


R = H, 1d; Me, 1e.
+ PMe3
- CO
+ P(t-Bu)3
+ CO
+ excess
PMe3
2f
R =H, 5a; Me, 5b
3f
4a
4b

Scheme 2.2

3f has the identical diaxial disposition of the two PMe_3 ligands (Scheme 2.2).

The elemental analysis and mass spectrum of **4a** and **4b** were identical and consistent with the formulation $Os(CO)_2(PMe_3)_2(COC_2H_2)$ and indicating an isomeric relationship between the two compounds. The IR spectra showed the presence of two terminal carbonyl bands (**4a**: 1996, 1932; **4b**: 2010, 1938) and a band around 1650 cm^{-1} (**4a**: 1652; **4b**: 1649) implying the presence of an acyl group as well, the low frequency being in accord with an α,β-unsaturated ketone.[32-35] Based on the relative intensity of the two terminal IR bands of **4a** and **4b**, the angles between the two carbonyls in **4a** and **4b** are calculated to be 104° and 93°, respectively.[36] Further evidence for the presence of the CHCHC(O) group is seen in the ^1H NMR spectra of both **4a** and **4b** (Table 2.1).

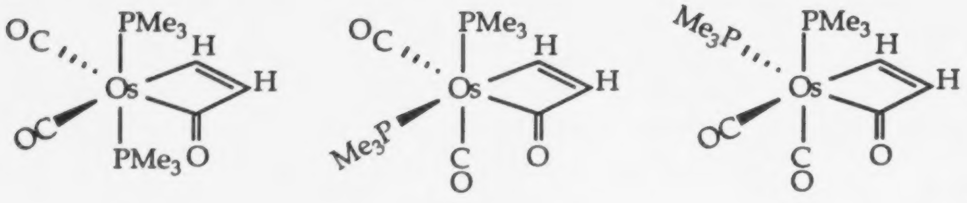
Table 2.1: Selected ^1H NMR Data for 4a and 4b

Compound	H_α	H_β	$^3J_{H\text{-}H}{}^a$
$\{\eta^2\text{-}C_2H_2C(O)\}Os(CO)_2(PMe_3)_2$ (**4a**)	8.41	8.65	6.9
$\{\eta^2\text{-}C_2H_2C(O)\}Os(CO)_2(PMe_3)_2$ (**4b**)	8.34	8.83	6.2
$\{\eta^2\text{-}C_2H_2C(O)\}Os(CO)_4Ru(CO)_4{}^b$	7.46	8.17	9.0

---

a Couplings in Hz. b[20]

By analogy with organic α,β-unsaturated ketones, the two hydrogens are assigned as α hydrogen and β hydrogen, where the β hydrogen resonates further downfield of the α hydrogen. Based on these data, there are three most likely structures as shown in Scheme 2.3.



E F G

Scheme 2.3

The single resonance at δ - 41.5 observed in the $^{31}P\{^1H\}$ NMR spectrum of **4a** is consistent with structure **E**. The $^{13}C\{^1H\}$ NMR spectrum of **4a** showed two triplets at δ 186.5 ($^2J_{CP}$ = 7.3 Hz) and 185.3 ($^2J_{CP}$ = 6.0 Hz) due to the terminal carbonyls. The third triplet at δ 213.4 is assigned to the acyl moiety. Two triplets at δ 166.7 ($^3J_{C_\alpha P}$ = 7.1 Hz) and 159.9 ($^2J_{C_\beta P}$ = 12.5 Hz) are assigned the α and β carbons of the $C_\beta HC_\alpha HC(O)$ group since $^2J_{C_\beta P}$ is generally larger than $^3J_{C_\alpha P}$ in this type of complexes. In the ^1H coupled spectrum extra doublet splittings for both α and β carbons were seen due to $^1J_{C_\alpha H}$ = 148.6 Hz and $^1J_{C_\beta H}$ = 149.0 Hz; the values are similar to that in ethylene ($^1J_{CH}$ = 156 Hz).[37] The resonance at δ 18.2 is assigned to the remaining PMe_3 carbons; its appearance is a pseudotriplet due to virtual coupling and there is a further quartet splitting in the ^1H coupled spectrum due to $^1J_{CH}$ = 127.1 Hz which is similar to that for ethane ($^1J_{CH}$ = 125 Hz).[37] The APT experiment is also in accord with these assignments. Thus the spectroscopic data clearly establish that compound **4a** has structure **E**.

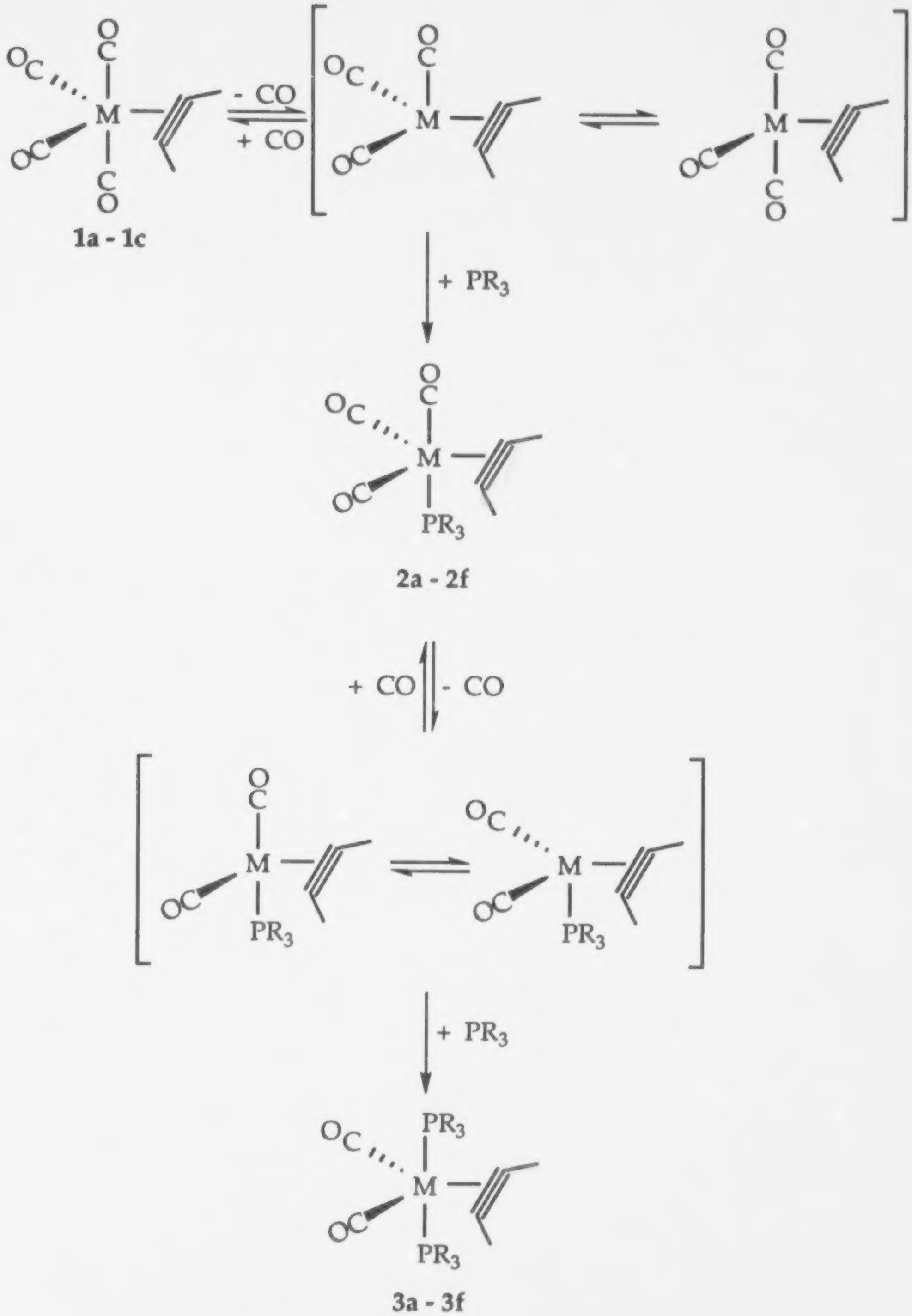
The $^{31}P\{^1H\}$ NMR spectrum of **4b** contained two resonances at δ - 44.4 and - 50.1, indicating different PMe_3 ligands. The $^{13}C\{^1H\}$ NMR spectrum showed two carbonyl bands at δ 188.3 ($^2J_{CP}$ = 89.7 Hz, $^2J_{CP}$ = 7.7 Hz) and 186.5 ($^2J_{CP}$ = 9.7 Hz, $^2J_{CP}$ = 4.9 Hz). The strong coupling ($^2J_{CP}$ = 89.7 Hz) of the carbonyl at δ 188.3 with one phosphine indicates their *trans* arrangement. The resonance at δ 207.8 ($^2J_{CP}$ = 11.4 Hz, $^2J_{CP}$ = 3.7 Hz) is assigned to the acyl carbon. The small coupling constants is more consistent with the acyl being *cis* to both phosphines instead of a *trans/cis* relation and hence structure **F** is favored for **4b**. Two resonances at δ 166.3 ($^3J_{C_\alpha P}$ = 6.5 Hz) and 154.7 ($^2J_{C_\beta P}$ = 43.8 Hz, $^2J_{C_\beta P}$ = 13.3 Hz) are assigned to the α and β carbons of the $C_\beta HC_\alpha HC(O)$ group. Selective ^{31}P decoupling experiments showed that the β-carbon is coupled to the phosphine at δ - 50.1 with a coupling constant of 43.8 Hz, indicating their *trans* disposition. Two more resonances at δ 20.0 and 16.0 are assigned to the two inequivalent PMe_3 ligands. Thus the spectroscopic data are in accord with the structure **F** (Scheme 2.2). It is to be noted that the assignments of the α and β carbons of the $C_\beta HC_\alpha HC(O)$ group of **4a** and **4b** are further corroborated by the similarities of the cis ^{31}P-^{13}C coupling constants; β: 12.5 Hz (**4a**), 13.3 Hz (**4b**) and α: 7.1 Hz (**4a**), 6.5 Hz (**4b**).

Although the reaction of compound **1d** with one equivalent trimethylphosphine cleanly and exclusively gave the monosubstituted product **2f**, the reaction of **1d** and **1e** with one equivalent $P(^tBu)_3$ unexpectedly gave products $Os(CO)_3\{\eta^2\text{-}C(O)C_2R_2C(O)\}(P(^tBu)_3)$ (**5a, 5b**) (Scheme 2.2). Since both **5a** and **5b** show similar spectroscopic features, only one will be discussed here. Consistent with mono-$P(^tBu)_3$ substitution, compound **5b** displayed three terminal carbonyl stretches (2078, 2012, 1994 cm^{-1}). However, the observation of a band at 1608 cm^{-1} indicated the presence of an acyl group as well. This was confirmed by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectrum showed two resonances at δ 179.8 ($^2J_{CP}$ = 10.6 Hz), and 173.2 ($^2J_{CP}$ = 68.8 Hz) for the terminal carbonyls and another one at δ 242.9 ($^2J_{CP}$ = 7.8 Hz) for the acyl moieties. Surprisingly the intensity ratio of the resonances was 2 : 1 : 2. The carbonyl at δ 173.2 is assigned to *trans* to the phosphine due to their strong coupling (68.8 Hz) whereas the other two equivalent carbonyls at δ 179.8 are *cis* to the phosphine due to their small coupling constant (7.8 Hz). In addition, a resonance at δ 168.2 is attributed to the carbons of alkene moiety in the {C(O)CMe=CMeC(O)} group. Therefore, compound **5b** is a *double* CO insertion product as shown in Scheme 2.2. Further support of the symmetrical structure came from the observation of only one singlet for the methyl group in the ^1H and $^{13}C\{^1H\}$ NMR spectrum. Thus the IR and NMR spectroscopic data clearly establish that the species **5b** has the structure as illustrated in Scheme 2.2.

2.2.3. Pathways for CO Substitution and Insertion Processes

As described above, the reactions of $M(CO)_4(\eta^2\text{-alkyne})$ complexes with monophosphines results in both simple CO substitution reaction and CO insertion into the metal-alkyne bonds. With electron poor alkynes, such as HFB and TFP, a second CO can also be substituted. On the other hand, complexes containing electron rich alkynes, such as C_2H_2 and C_2Me_2, also undergo CO insertions. Thus pathways for the formation of the two distinct products will be discussed separately.

CO Substitution Reactions. The initial sixteen-electron species is formed by CO dissociation (Scheme 2.4). There are two possibilities for the generation of the four-coordinate $[M(CO)_3(\eta^2\text{-alkyne})]$ intermediate; CO dissociation either from the axial or from the equatorial position of the trigonal bipyramidal ground state structure. Hoffmann has shown that, in


- CO
+ CO
1a - 1c
+ PR$_3$
2a - 2f
+ CO
- CO
+ PR$_3$
3a - 3f

Scheme 2.4

trigonal bipyramidal d^8 ML_5 complexes, π-backbonding is stronger, but σ-bonding is weaker in the equatorial plane.[38] Thus whether an axial or equatorial CO ligand is more labile depends on the relative strength of σ and π bonding. In $M(CO)_4(\eta^2\text{-alkyne})$ complexes the situation are more complicated because of the four-electron destabilization by the alkyne ligand; whether the axial or equatorial CO's are destabilized more is not obvious. Structural studies on $M(CO)_4(\eta^2\text{-alkyne})$ complexes show that the axial and equatorial M-CO bonds are of nearly the same length.[18,39] Although the site preference for CO dissociation in **1** is not clear, the generated $[M(CO)_3(\eta^2\text{-alkyne})]$ intermediates are significantly different (Scheme 2.4). There are several related and structurally characterized examples of $ML_3(\eta^2\text{-alkyne})$ complexes, where M is a d^8 transition metal (M = Pt (II); Co (I), Ir (I); Ru (0), Os (0)).[39] These complexes adopt a structure with approximate C_s symmetry, which we believe is very similar to the putative $[M(CO)_3(\eta^2\text{-alkyne})]$ intermediate generated from an axial CO dissociation as shown in Scheme 2.4. One of such structures, $Os(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2$, is shown in Figure 2.2.[40] Theoretical calculations established that four electron donation from the alkyne ligand is responsible for both the unusual structure and the stability of these species.[39] Since the intermediate from equatorial CO dissociation requires additional rearrangement to generate this structure, a process involving CO dissociation from axial position is favored.

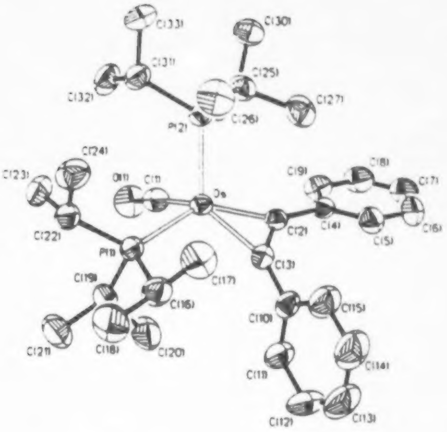
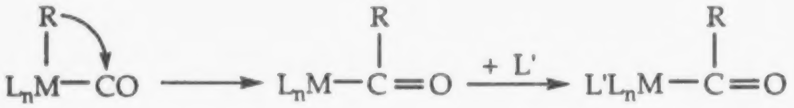


Figure 2.2: Molecular Structure of $Os(\eta^2\text{-}C_2Ph_2)(CO)(P^iPr_3)_2$

The intermediate $[M(CO)_3(\eta^2\text{-alkyne})]$ species then reacts with phosphine to form compounds **2** (Scheme 2.4). These compounds can undergo further CO dissociation to give the $[M(CO)_2(PR_3)(\eta^2\text{-alkyne})]$ intermediate. According to Atwood and Brown's site preference arguments,[25-27,41] equatorial CO dissociation should occur more readily than axial CO dissociation. This is due to the fact that a stronger σ donor and weaker π acceptor ligand than CO, such as phosphine, strengthens the M-CO bond *trans* to it. Thus the so called "cis-effect" of PR_3 directs *cis* CO dissociation by strengthening the M-CO bond in the *trans* position. To account for the geometry of the final disubstituted product, it is assumed that this species rearranges to a structure similar to $[M(CO)_3(\eta^2\text{-alkyne})]$ described above, and then adds phosphine. On the other hand, the so far not fully appreciated cis-effect of two-electron alkyne ligands could assist axial CO dissociation again and generate directly the intermediate with proper geometry to add phosphine. The common feature for both monosubstituted species **2** and disubstituted species **3** is that phosphine ends up in the axial position(s), which is in accord with Rossi and

Hoffmann's theoretical calculations.[38] On the basis of symmetry and overlap arguments, Rossi and Hoffmann have shown that for d^8 trigonal-bipyramidal transition metal complexes stronger σ-donor and weaker π-acceptor ligands prefer the axial site. There are numerous examples to support this site preference. For instance, substitution reactions of $M(CO)_5$ (M = Fe, Ru, Os) with PR_3 yield the mono- and disubstituted compounds with phosphine occupying the axial position(s).[42-47]

CO Insertion Reactions. The mechanism of CO insertion into the metal-carbon σ-bond has been extensively studied.[48,49] Although two mechanisms involving either alkyl migration or CO insertion have been observed, the former is much more common. Calderozzo[50] and Flood[51] have studied the carbonylation of $(CH_3)Mn(CO)_5$ by IR and ^{13}C NMR spectroscopy. By careful analysis of the product distribution, it is clear that the "insertion" process involves migration of the methyl group to a *cis* CO ligand.



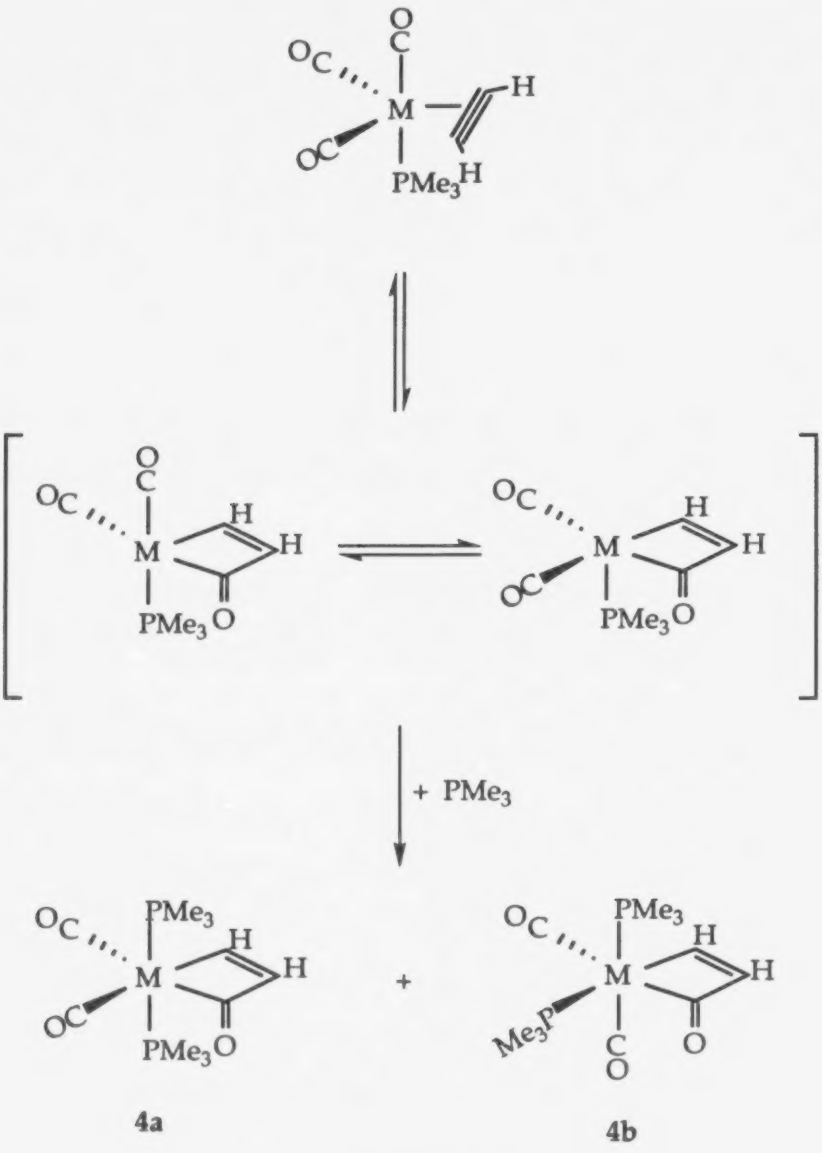
$$\mathrm{L_n\overset{R}{M}{-}CO} \longrightarrow \mathrm{L_nM{-}\overset{R}{C}{=}O} \xrightarrow{+\ L'} \mathrm{L'L_nM{-}\overset{R}{C}{=}O} \qquad (2.3)$$

As shown in eq. 2.3, the rate-determining step is alkyl migration to form the $[L_nM(C(O)R)]$ intermediate, followed by addition of an incoming nucleophile (L') to restore the 18-electron configuration of the metal center and complete a two-step process. Consequently the strength of the metal-alkyl bond plays an important role in the process. It has been found that alkyl groups bearing electron-donating substituents facilitate the reaction while those with electron-withdrawing substituents retard it.[52,53]

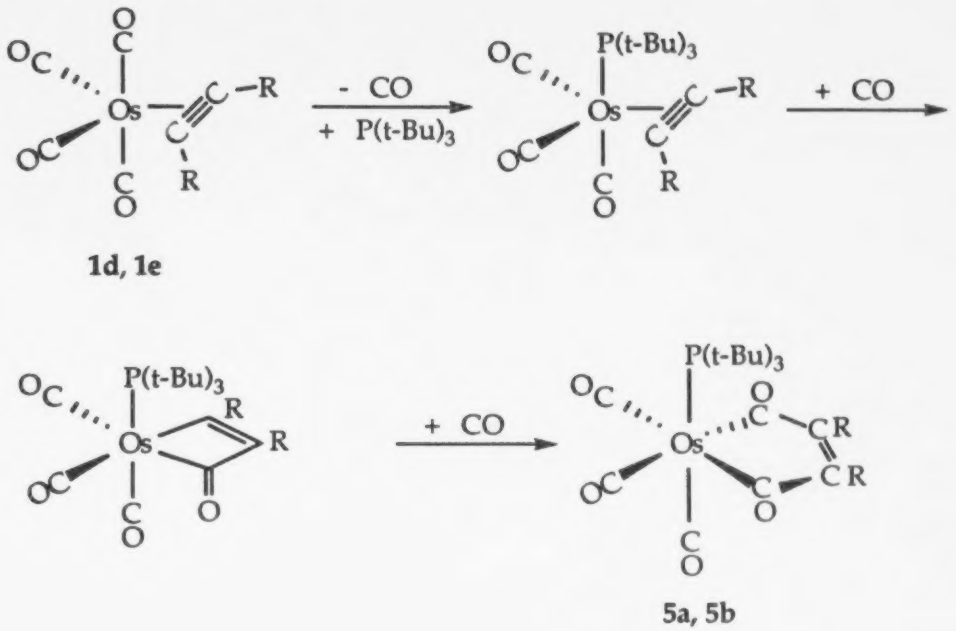
Scheme 2.5 depicts the proposed pathway for CO "insertion" reaction of $Os(CO)_4(\eta^2-C_2H_2)$ induced by PMe_3. Since PMe_3 is a strong σ donor, it increases the electron density of the metal center and enhances the four electron destabilization between the filled d_{yz} orbital of the metal and the filled $\pi_{\perp}$ orbital of the alkyne. This filled-filled interaction weakens the metal-alkyne bond and promotes the migratory insertion. It is interesting that addition of the second PMe_3 ligand generates two isomeric compounds **4a** and **4b**.

Another question is whether CO insertion occurs after the disubstituted species **3f** has been generated. This possibility can be ruled out since **3f** does not insert CO. As will be described later (section 2.2.4), it undergoes facile oxidative addition to give compound **6**.

Unexpectedly, the reactions of compounds **1d** and **1e** with $P(^tBu)_3$, gave double CO inserted products **5a** and **5b**. A consecutive CO "insertion" pathway is proposed (Scheme 2.6). Several important features require some comments. First, since the final products have one more CO ligand than the starting materials, the additional CO must come from another osmium species which ultimately decomposes. Second, although the electronic properties of the two phosphines, $P(^tBu)_3$ and PMe_3, are similar, a second CO "insertion" takes place with the bulky $P(^tBu)_3$. Thus steric effects seem to be operative as well. Possibly unfavorable interactions between the $P(^tBu)_3$ and the four-membered ring are relieved by formation of the five-membered ring. Third, a preliminary study showed that, the reaction of **1d** with $P(^tBu)_3$ under CO atmosphere gave the product **5a** after 4.5 h at 0°C. Since this reaction did not go to completion under these conditions, and as the reaction under N_2 atmosphere was completed within 2.5 h at 0°C, the rate of the reaction under CO atmosphere is, apparently, much slower than that under N_2 atmosphere.


OC
CO
M
H
PMe3
+ PMe3
4a
4b
Me3P

Scheme 2.5



1d, 1e

5a, 5b

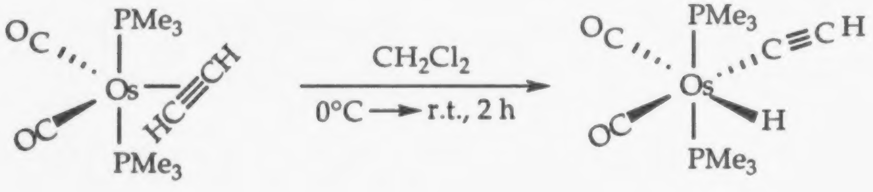
Scheme 2.6

2.2.4 Thermal Stability of the Phosphine Adducts

As described in Chapter 1, the stability of $Os(CO)_4(\eta^2\text{-alkyne})$ complexes depends on the alkyne. The general trend is that a complex containing an electron poor alkyne is more stable than that containing an electron rich alkyne. This is mainly attributed to the four electron destabilization in the ground state; the π-acceptor ability of electron poor alkyne results in less repulsion and hence increased stability. A way of removing the four electron interaction is to insert CO, the so formed CHCHC(O) moiety functions as a two electron donor. Indeed, the CO inserted products are stable at room temperature. The four-electron destabilization remains in the simple phosphine substitution complexes implying possible further transformations. This is, in fact, seen for $Os(CO)_3(PMe_3)(\eta^2\text{-}C_2H_2)$ and $Os(CO)_2(PMe_3)_2(\eta^2\text{-}C_2H_2)$.

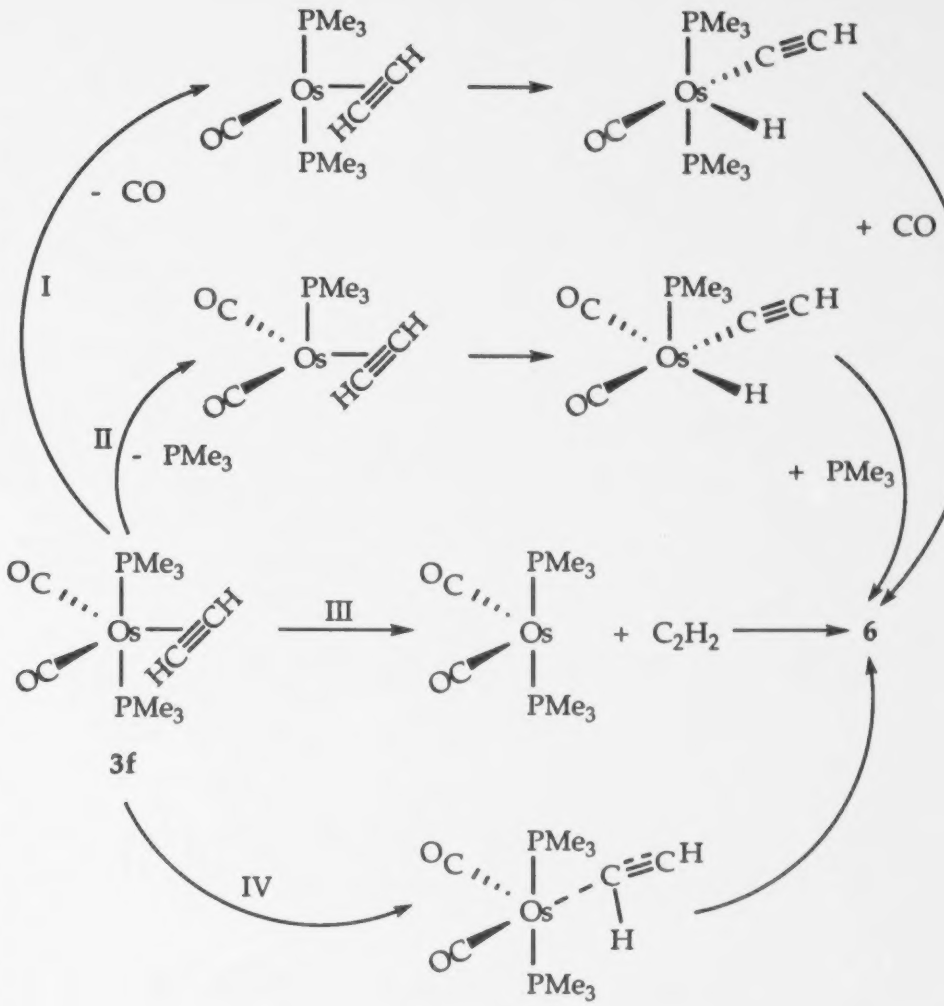
(a) Transformation of $Os(CO)_2(PMe_3)_2(\eta^2\text{-}C_2H_2)$, 3f

When a dichloromethane solution of compound **3f** was warmed to ambient temperature, a new species **6** was formed (eq. 2.4). The ^1H NMR spectrum showed two triplets at δ - 7.70 and 1.51 in a ratio of 1:1. The high field triplet at δ - 7.70 is assigned to the hydride whereas the signal at δ 1.51 is attributed to the acetylide hydrogen.[54,55] In the ^{13}C NMR spectrum, two triplets at δ 182.5 and 181.1 are in the terminal carbonyl region, while the two triplets at δ 93.4 ($^3J_{CP}$ = 7.7 Hz) and 87.0 ($^2J_{CP}$ = 17.2 Hz) are due to the carbon atoms of the acetylide group. The remaining triplet at δ 21.0 is due to the carbon atom of the PMe_3 methyl group, and the pseudotriplet appearance is ascribed to virtual coupling. Thus the NMR data obtained clearly establish the structure of compound **6** (2.4).



3f **6** (2.4)

As illustrated in Scheme 2.7, there are four possible pathways for formation of **6**. Mechanisms I and II are unlikely since the intermediates generated should undergo phosphine or carbon monoxide addition rather than oxidative addition when the reactions are performed using large excess (100 equivalent) PMe_3 or under CO atmosphere, no such substitutions were seen. Mechanism III can also be eliminated because the reactions under large excess PMe_3 or under CO atmosphere would give a


PMe3
Os
OC
HC≡CH
C≡CH
H
- CO
+ CO
I
II
- PMe3
+ PMe3
III
+ C2H2
6
3f
IV

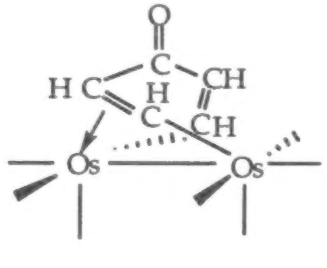
Scheme 2.7

substitution product instead of **6**. Thus the intramolecular isomerization mechanism IV is most likely operative here. Theoretical calculations show that such a pathway, by slippage of the alkyne to an η^1 geometry, is the initial step for alkyne to vinylidene isomerization in $CpMn(CO)_2(HC_2R)$ complexes.[56] In addition, there are several examples of alkyne isomerization to hydrido-acetylide species.[57-59] The facile alkyne-to-hydrido-acetylide isomerization is again attributed to elimination of four electron destabilization in $Os(CO)_2(PMe_3)_2(\eta^2\text{-}C_2H_2)$ (**3f**).

(b) Transformation of $Os(CO)_3(PMe_3)(\eta^2\text{-}C_2H_2)$, 2

The reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with one equivalent PMe_3 at 0°C in pentane gives the complex **2f** almost quantitatively.[31] When this solution was warmed to room temperature and maintained at this temperature for 12 h, an orange suspension was obtained. After removal of the solvent, recrystallization from hexane the new product **7** was isolated in 59% yield.

Elemental analysis and mass spectrum of this product is in agreement with the formula $Os_2(CO)_5(PMe_3)_2(COC_4H_4)$ indicating the formation of a dinuclear species. This composition is reminiscent of the well known "flyover" pentadienone complexes, $M_2(CO)_{6-n}L_n\{\mu\text{-}\sigma:\eta^4\text{-}(C_2R_2)_2CO\}$ (M = Fe, Ru; L = PPh_3, n = 1, 2; R = CH_3, Ph, H),[60-62] except that there is one more carbon monoxide in this case. Thus a similar structure is proposed for species **7**, but with coordination of only one of the double bonds of the "flyover" bridge (Scheme 2.8).



Scheme 2.8

The IR spectrum showed five terminal carbonyl bands (1940 - 2055 cm^{-1}) and one band at 1605 cm^{-1}. When the experiment was repeated using

$Os(^{13}CO)_4(\eta^2\text{-}C_2H_2)$, the IR spectrum showed that all six bands shifted to lower frequency, indicating that they are due to CO absorption. Thus the band at 1605 cm^{-1} is assigned to the acyl group. As shown in Table 2.2, the acyl band of 7 is shifted to lower frequency compared to the other flyover compounds. This is attributed to the delocalization of the electron density in the remaining α,β-unsaturated ketones of 7.[60] In the case of diruthenium and diiron flyover pentadienone complexes, both double bonds are coordinated to the metal center hence the stretching frequency is similar to ketones.

Table 2.2: IR Data for 7 and Related Compounds

Compound	$\upsilon_{(acyl)}$ (cm^{-1})
$Ru_2(CO)_6\{\mu\text{-}\sigma\text{:}\eta^4\text{-}(CPhCMe)_2CO\}$	1681[a]
$Fe_2(CO)_5(PPh_3)\{\mu\text{-}\sigma\text{:}\eta^4\text{-}(CPhCMe)_2CO\}$	1657[a]
$Os_2(CO)_5(PMe_3)_2\{\mu\text{-}\sigma\text{:}\eta^2\text{-}(CHCH)_2CO\}$ 7	1605

---

[a] 61

The $^{31}P\{^1H\}$ NMR spectrum of 7 showed two distinct singlets at δ - 31.2 and - 51.1. For the convenience of further discussion, P_a is used to stand for the resonance at δ - 31.2 and P_b for the other phosphine. In the ^1H NMR spectrum four resonances at δ 9.30, 8.79, 6.25, and 4.65 integrating as one hydrogen each and two resonances at δ 1.88 and 1.83 integrating as nine hydrogens each were observed. They are assigned to the acetylenic and PMe_3 protons respectively. Selective ^{31}P decoupling experiments have clearly established that the signals at δ 9.30, 6.25, and 1.83 are associated with P_a whereas the signals at δ 8.79, 4.65, and 1.88 are associated with P_b. This indicates that the two phosphines (P_a and P_b) are bound to the different osmiums rather than the same osmium center as one would expect that in the latter case at least some of the acetylenic hydrogen signals would be coupled to both phosphines.

Table 2.3: Selected ^1H NMR Data for 7 and Related Compounds with Coordinated Pentenone Double Bond

Compound	$\delta_{H\alpha}$	$\delta_{H\beta}$	$^3J_{H-H}$
$\{\mu\text{-}\eta^1{:}\eta^2\text{-}(C_2H_2)_2CO\}Os_2(CO)_5(PMe_3)_2$ 7	4.65	8.79	9.3
$\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_2H_2C(O)\}Ru(CO)_5(\mu\text{-dppm})^a$	4.59	8.19	8.5
$\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_2H_2C(O)\}Ru_2Cp_2(CO)_2{}^b$	3.42	10.94	7.0
$\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_2H_2C(O)\}OsRhCp(CO)_3PMe_2Ph^c$	4.72	8.82	6.3

---

a[62], b[63], c[64]

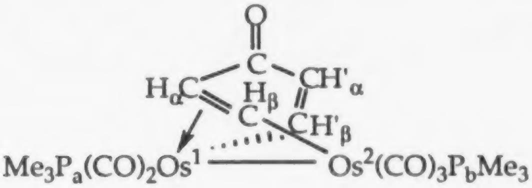
Table 2.4: Selected ^1H NMR Data for 7 and Related Compounds with Uncoordinated Pentenone Double Bond

Compound	$\delta_{H'\alpha}$	$\delta_{H'\beta}$	$^3J_{H-H}$
$\{\mu\text{-}\eta^1{:}\eta^2\text{-}(C_2H_2)_2CO\}Os_2(CO)_5(PMe_3)_2$ 7	6.25	9.30	12.6
$\{\mu\text{-}\eta^1{:}\eta^1\text{-}C_2H_2C(O)\}OsRu(CO)_8{}^a$	7.46	8.17	9.0
$\{\mu\text{-}\eta^1{:}\eta^1\text{-}C_2H_2C(O)\}OsIrCp(CO)_5{}^b$	7.51	7.98	9.1
$\{\mu\text{-}\eta^1{:}\eta^1\text{-}C_2H_2C(O)\}Ru_2(CO)_4(dppm)_2{}^c$	7.4	8.0	9.8

---

a[20], b[65], c[66]

As shown in the proposed structure 7, there are two types of α, β-unsaturated units linked to the CO moiety. One of the alkene groups is coordinated to the metal center (type A), while the other remains free (type B). It is well known that, for both types of structures, the β-hydrogen is greatly deshielded[20,65,66] whereas the α-hydrogen resonates at very different frequencies. As shown in Table 2.3 and 2.4, one set of hydrogens at δ 8.79 and 4.65 have features similar to type A, while the other set at δ 9.30 and 6.25 resembles type B. Thus, we can conceive the following structure for 7 where P_a and P_b are bound to Os^1 and Os^2, respectively. However the geometrical arrangement around each osmium remains to be determined.



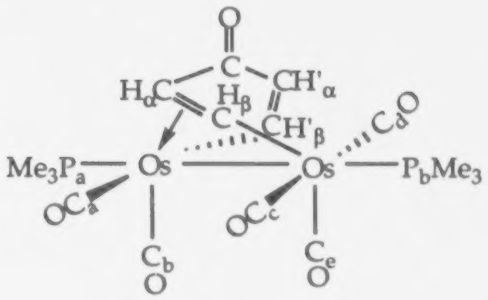
7

The $^{13}C\{^1H\}$ NMR spectrum showed six resonances at δ 202.0, 191.1, 189.5, 188.4, 183.8, and 180.5 with a intensity ratio of 1:1:1:1:1:1. The low field singlet at δ 202.0 is assigned to the acyl while the other five resonances are attributed to the terminal carbonyls. Four resonances at δ 173.8, 134.9, 131.9, and 64.9 are due to the carbon atoms of the ring. This has been corroborated by the ^1H coupled ^{13}C NMR experiment, where the resonances at δ 173.8 ($^1J_{CH}$ = 132 Hz), 134.9 ($^1J_{CH}$= 141.7 Hz), 131.9 ($^1J_{CH}$ = 155.3 Hz), and 64.9 ($^1J_{CH}$ = 151.9 Hz) exhibit one bond C-H couplings.[37] The remaining resonances at δ 22.6 and 19.5 are from the carbon atoms of the two PMe_3 groups. An APT experiment is also in accord with these assignments. Selective ^{31}P decoupling experiments have established that the carbonyl resonances at δ 189.5 and 183.8 are associated with P_a while the resonances at δ 191.1, 188.4, and 180.5 are associated with P_b. In addition, the small coupling constants (5 - 9 Hz) between the phosphine and carbonyl ligands indicate that they are *cis* to one another. The $^{13}C\{^1H\}$ NMR spectrum of compound 7, prepared from $Os(^{13}CO)_4(\eta^2\text{-}C_2H_2)$, showed that the carbonyls at δ 191.1 and 188.4 are coupled each other with a coupling constant of 34.5 Hz, indicating that they are located in *trans* positions.[67] The ring carbon resonances at δ 131.9 and 64.9 showed strong couplings to the acyl moiety ($^1J_{C\text{-}C(O)}$: 55.8 and 49.7 Hz, respectively) in the typical range for one bond coupling.[37,66] This suggests that these two resonances are the carbons directly bound to the acyl while the other two resonances at δ 173.8 ($^2J_{(C\text{-acyl})}$ = 17.7) and 134.9 ($^2J_{(C\text{-acyl})}$ = 21.5 Hz) are due to the carbon atoms bound to the metal centers. In order to further determine the relationship between the ring carbon atoms and the hydrogens, a $^1H\text{-}^{13}C$ shift-correlated 2D NMR experiment was carried out (Table 2.5). The chemical shifts of C_α and C_β are in the typical range of type A[62,63] whereas the chemical shifts of C'_α and C'_β are in agreement with those of type B.[20,65]

Table 2.5: The ^1H - ^{13}C Shift-correlated 2D NMR Data for 7

	$C_\alpha H_\alpha$	$C_\beta H_\beta$	$C'_\alpha H'_\alpha$	$C'_\beta H'_\beta$
$\delta(^{13}C)$	64.9	134.9	131.9	173.8

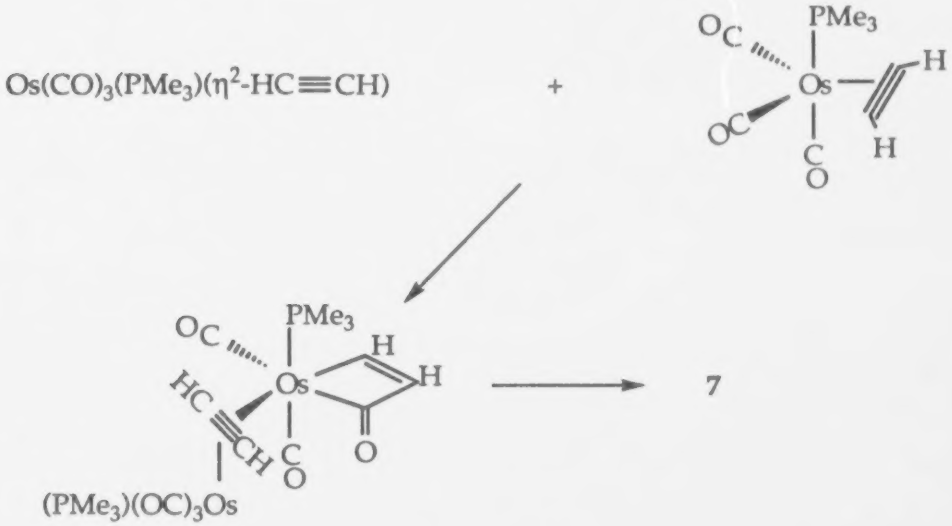
Although suitable crystals of compound 7 for X-ray structure determination could not be obtained, the IR and NMR spectroscopic data unambiguously establish the structure of compound 7. The CO assignments are shown in Scheme 2.9.


O
C
$H_\alpha C$
H_β
CH'_α
C
CH'_β
C_dO
Me_3P_a
Os
Os
P_bMe_3
OC_a
OC_c
C_b
O
C_e
O

7

Scheme 2.9

The formation of compound **7** can be envisioned as illustrated in Scheme 2.10. The initial step is CO insertion, thus creating a coordination site, followed by addition of the second molecule $Os(CO)_3(PMe_3)(\eta^2\text{-}C_2H_2)$ through alkyne coordination. Coupling between the coordinated alkyne and the acyl, followed by rearrangement gives complex 7.


$Os(CO)_3(PMe_3)(\eta^2\text{-}HC\equiv CH)$
+
PMe3
OC
Os
H
OC
C
O
H
PMe3
OC
H
Os
H
HC
CH
C
O
O
$(PMe_3)(OC)_3Os$
7

Scheme 2.10

2.3. Conclusions

The compounds $M(CO)_4(\eta^2\text{-alkyne})$ have been shown to be very reactive towards monophosphines under mild conditions. The reactions generally yield two types of products; one is derived from CO substitution, the other from CO insertion. The compounds which contain an electron-poor alkyne, such as CF_3C_2H or $CF_3C_2CF_3$, undergo both mono- and disubstitution. The complexes that contain an electron-rich alkyne, such as C_2H_2 or C_2Me_2, feature both CO substitution and CO insertion. The CO inserted complexes are the first clear examples of coupling reactions between a coordinated CO and coordinated alkyne unit. In addition, compounds **4a** and **4b** are, to our knowledge, the first examples of metallacyclobutenones from simple acetylene. More surprisingly perhaps, the reaction of $Os(CO)_4(\eta^2\text{-alkyne})$ (alkyne = C_2H_2, C_2Me_2) with $P(t\text{-}Bu)_3$ produces the unusual osmacyclopentenediones, in which the metallacyclopentenedione species are derived from *double* CO insertions.

Although two types of products are obtained, all the reactions proceed by initial CO loss. The facile CO dissociation is attributed to the four electron destabilization in the ground state and four electron stabilization of the putative $[Os(CO)_3(\eta^2\text{-alkyne})]$ intermediate. With complexes containing an electron-poor alkyne, substitution of a second CO occurs. In some cases, it appears that the rate of the second CO substitution is faster than the first, and this is rationalized in terms of cis labilization by the coordinated monophosphine. With compounds that contain an electron-rich alkyne, on the other hand, CO insertion takes place due to the weak metal-alkyne bonds. The double CO insertion observed with the bulky $P(t\text{-}t\text{-}Bu)_3$ indicates that steric effect also plays an important role in the process.

The CO inserted products are stable at room temperature due to elimination of the effect of the four electron alkyne. However, the complexes $Os(CO)_2(PMe_3)_2(\eta^2\text{-}C_2H_2)$ and $Os(CO)_3(PMe_3)(\eta^2\text{-}C_2H_2)$, undergo further transformations. In the former case facile oxidative-addition occurs to give compound **6** by intramolecular isomerization. In the later case, a dinuclear compound **7** is generated from the coupling of two alkynes and a CO ligand. The ease of C-C bond formation, originated from *two metal centers*, is evident and provides a model for several metal carbonyl mediated reactions involving alkynes and carbon monoxide.[2,4,68-70]

2. 4 Experimental Section

2. 4. 1 Solvents and General Techniques

All solvents were dried and distilled from the appropriate dying agents listed in Table 2.1. Deuterated solvents were also dried and degassed by freez-pump-thaw cycles and stored over molecular sieves under nitrogen. Pentane was pretreated sequentially with concentrated sulphuric acid, aqueous solution of sodium bicarbonate, and distilled water before being dried over sodium sulphate and distilled from calcium hydride. The same procedure was used for purification of hexane except that distillation was from potassium metal.

Solvents	Drying Agent
Benzene	Potassium metal
Dichloromethane	Phosphorous pentoxide
Diethyl ether	Sodium benzophenone ketyl
Hexane	Potassium metal
Pentane	Calcium hydride
Toluene	Sodium benzophenone ketyl
Tetrahydrofuran	Sodium benzophenone ketyl

Table 2.6 Solvents and Drying Agents

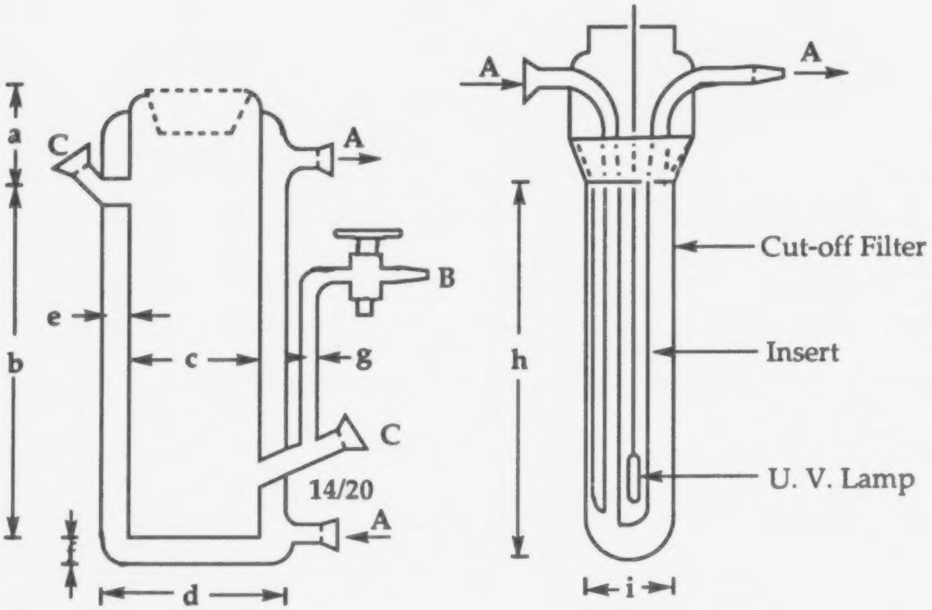
All glassware was pretreated with a KOH/C_2H_5OH (95%) solution and a dilute HCl solution, respectively. This was followed by cleaning with distilled water and drying at 250°C overnight before use. All reactions were carried out under argon or nitrogen atmosphere using standard Schlenk procedures. The argon or nitrogen was purified by passing it through a heated (100°C) column of BASF Cu catalyst (R3 - 11) to remove any trace of oxygen and a column of Mallinkrodt Aquasorb (P_2O_5 on an inert support) to remove traces of water. All gases were used as received unless otherwise stated.

2. 4. 2. Physical Measurements

Infrared spectra were recorded on a Bomem MB-100 Fourier transform spectrometer over the range 2200 - 1500 cm^{-1}. Solution samples and background solvent were held between KBr (0.1 mm) plates. The ^1H, ^{31}P, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AM-400, Bruker AM-300, or a Bruker WH-200 spectrometer. The solvent was CD_2Cl_2, unless otherwise stated. Electron impact mass spectra were recorded on an A.E.I. MS-12 spectrometer operating at 70 ev. Fast Atom Bombardment (FAB) mass spectra were recorded on a modified A.E.I. MS-9 spectrometer operating at 1500 RP and 10 sec/decade using either Cleland or 3-nitro-benzylalcohol (NBA) as sample matrix. Elemental analysis were performed by the microanalytical service of the Chemistry Department.

2. 4. 3. Photochemical Techniques

Photochemical experiments at low temperatures were carried out in a photolysis reactor as shown in Figure 2.1. The reactor consisted of an outside cooling jacket and a cooling insert. The system was cooled and maintained at a constant temperature (from 0°C to - 70°C) by a MGM Lauda Circulating Bath with methanol as a circulating/cooling solution. A Philips HPK 125 Watt mercury vapour lamp was used as the irradiation source. The wavelength of the radiation was controlled by cut filters such as GWV (Glasswerk Wertheim) glass ($\lambda \geq 370$ nm).



A: inlet/outlet cooling ports

B: gas inlet

C: sample ports

a: 3.0 cm
b: 12.0 cm
c: 4.5 cm
d: 7.0 cm

e: 1.25 cm
f: 1.0 cm
g: 0.5 cm
h: 13.5 cm
i: 3.0 cm

Figure 2.3: Internal Photolysis Apparatus

Figure 2.2 shows a typical external photolysis apparatus used in our laboratory. This system was used for the photolysis at room temperature. Tap water was used to keep the lamp cool. Like the internal photolysis, an appropriate cut-off filter was selected and a sample solution in a Schlenk tube was positioned beside the insert.

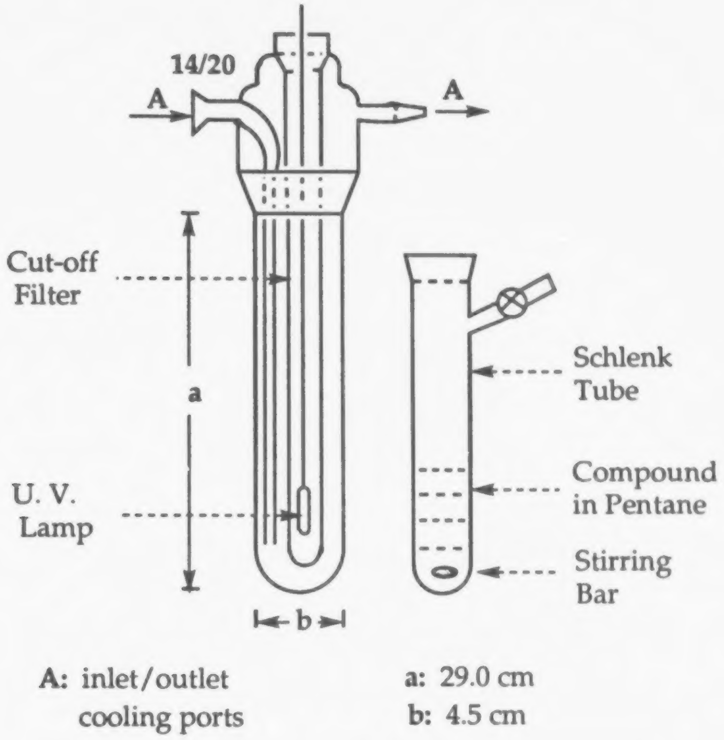

14/20
A
A
Cut-off Filter
a
U. V. Lamp
b
Schlenk Tube
Compound in Pentane
Stirring Bar
A: inlet/outlet cooling ports
a: 29.0 cm
b: 4.5 cm

Figure 2.4: External Photolysis Apparatus

2.4.4. Starting Materials and Reagents

Acetylene was purchased from Linde Gas Products and was passed through a dry ice/acetone trap to remove acetone stabilizer. The ^{13}CO (99%) was purchased from Isotec, Inc. The gaseous alkynes, CF_3C_2H and $CF_3C_2CF_3$, were purchased from Farchan Chemical Co., while MeC_2Me, PMe_3, PPh_3, $P(^tBu)_3$, and $Os_3(CO)_{12}$, were purchased from Aldrich Chemical Co., and $RuCl_3$ was purchased from Johnson Matthey Inc. The following compounds were prepared by published procedures: $Ru_3(CO)_{12}$,[71] $Ru(CO)_5$,[72] $Ru(CO)_4(\eta^2\text{-}CF_3C_2CF_3)$,[19] $Os(CO)_5$,[73] $Os(CO)_4(\eta^2\text{-}C_2H_2)$,[20] $Os(CO)_4(\eta^2\text{-}CF_3C_2CF_3)$,[19] and $Os(CO)_4(\eta^2\text{-}MeC_2Me)$.[74]

2.4.5. Synthetic Procedures

Synthesis of $Os(CO)_3(PMe_3)(\eta^2\text{-}CF_3C_2CF_3)$, 2a

Trimethylphosphine (11.2 µl, 0.108 mmol) was added to a solution of $Os(CO)_4(\eta^2\text{-HFB})$ **1a** (50 mg, 0.108 mmol) in pentane (10 mL) at 0°C, the solution was stirred at this temperature for 5 h. The solution was then cooled to - 78°C and the solvent was removed in vacuo at - 78°C. Recrystallization from pentane at - 78°C afforded **2a** as a white powder (46 mg, 83%, mp: - 8°C). MS (FAB): M^+ - n CO, n = 0-3.

IR (pentane, cm^{-1}): υ_{CO}: 2086 s, 2013s, 1983 vs; $\upsilon_{C\equiv C}$: 1779 w.

^1H NMR: 1.46 (d, $^2J_{PH}$ = 10.0 Hz).

$^{31}P\{^1H\}$ NMR: - 43.5 (sept, $^4J_{PF}$ = 2.0 Hz).

^{19}F NMR: - 57.0 (d, $^4J_{PF}$ = 2.0 Hz).

$^{13}C\{^1H\}$ NMR: 179.2 (d, $^2J_{PC}$ = 10.6 Hz, 2 CO), 170.4 (d, $^2J_{PC}$ = 113.0 Hz, 1CO), 16.5 (d, $^1J_{PC}$ = 37.5 Hz, $P(CH_3)_3$).

Synthesis of $Os(CO)_3(PMe_3)(\eta^2\text{-}CF_3C_2H)$, 2b

Trimethylphosphine (21.6 µl, 0.208 mmol) was added to a pentane solution (25 mL) of $Os(CO)_4(\eta^2\text{-TFP})$ **1b** (82.5 mg, 0.208 mmol) at 0°C. After stirring for 14 h at 0°C, the colorless solution was cooled to - 78°C. The solvent was then removed under reduced pressure and the residue was recrystallized from pentane at - 78°C to give **2b** as a white powder (84 mg, 91%). The compound is a liquid at room temperature. Anal. Calcd. for $C_9H_{10}O_3F_3POs$: C, 24.33; H, 2.27. Found: C, 24.00; H, 2.18.

IR (pentane, cm^{-1}): υ_{CO}: 2074 s, 1998 s, 1967 s; $\upsilon_{C\equiv C}$: 1708 w.

^1H NMR: 6.93 (dq, $^4J_{HF}$ = $^3J_{HP}$ = 3.0 Hz, 1H), 1.35 (d, $^2J_{HP}$ = 10.5 Hz, 9 H).

$^{31}P\{^1H\}$ NMR: - 44.5 (q, $^4J_{PF}$ = 2.8 Hz).

^{19}F NMR: - 55.1 (dd, $^4J_{FH}$ = 3.0 Hz, $^4J_{FP}$ = 2.8 Hz).

$^{13}C\{^1H\}$ NMR: 182.8 (d, $^2J_{PC}$ = 10.6 Hz, 1CO), 181.2 (d, $^2J_{PC}$ = 10.4 Hz, 1 CO), 172.7 (d, $^2J_{PC}$ = 115.4 Hz, 1 CO), 15.8 (d, $^1J_{CP}$ = 36.6 Hz, $P(CH_3)_3$).

Characterization of $Os(CO)_3(PPh_3)(\eta^2\text{-}CF_3C_2CF_3)$, 2c

Reaction of **1a** with one equivelant of PPh_3 gave a mixture of compounds **2c** and **3c**. Although separation of these compounds was attempted by both sublimation and column chromatography, pure compound **2c** could not be obtained. Spectroscopic data were deduced after preparation of pure **3c**.

$^{31}P\{^1H\}$ NMR (0°C): 7.3 (sept, $^4J_{PF}$ = 1.9 Hz).

^{19}F NMR (0°C): - 55.4 (d, $^4J_{PF}$ = 1.9 Hz).

Characterization of $Ru(CO)_3(PMe_3)(\eta^2\text{-}CF_3C_2CF_3)$, 2d

The compound was observed by NMR spectroscopy from - 20°C to 0°C. It was not possible to obtain the pure product because the disubstituted product **3d** was formed much faster even when one equivalent PMe_3 was employed. The carbonyl signals was identified by using a ^{13}CO enriched sample.

^1H NMR (0°C): 0.99 (d, $^2J_{PH}$ = 2.1 Hz)

$^{31}P\{^1H\}$ NMR (0°C): - 4.98 (sept, $^4J_{PF}$ = 1.3 Hz)

^{19}F NMR (0°C): - 54.9 (d $^4J_{PF}$ = 1.3 Hz)

$^{13}C\{^1H\}$ NMR (0°C): 198.4 (d, $^2J_{PC}$ = 14.4 Hz, 2CO), 188.2 (d, $^2J_{PC}$ = 119.7 Hz, 1CO).

Synthesis of $Os(CO)_2(PMe_3)_2(\eta^2\text{-}CF_3C_2CF_3)$, 3a

Trimethylphosphine (22.3 µl, 0.216 mmol) was added to a colorless solution of $Os(CO)_4(\eta^2\text{-HFB})$ **1b** (50 mg, 0.108 mmol) in 10 mL pentane at room temperature. The reaction was stirred for 2 h. The solution was then cooled to - 78°C. The solvent was removed in vacuo at - 78°C to give a white solid which was recrystallized from pentane at - 78°C to give **3a** as a white powder (51 mg, 74%). Anal. Calcd. for $C_{12}H_{18}O_2P_2F_6Os$: C, 25.72; H, 3.24. Found: C, 25.80; H, 3.08.

IR (pentane, cm^{-1}): υ_{CO}: 1998 s, 1934vs; $\upsilon_{C\equiv C}$: 1750w.

^1H NMR ($CDCl_3$): 1.42 (t, J_{HP} = 3.8 Hz)

$^{31}P\{^1H\}$ NMR ($CDCl_3$): - 42.71 (sept, $^4J_{PF}$ = 3.06 Hz)

^{19}F NMR : - 55.2 (t, $^4J_{PF}$ = 3.06 Hz)

$^{13}C\{^1H\}$ NMR: 186.0 (t, ^2JPC = 7.8 Hz, CO), 17.9 (t, $^1J_{PC}$ = 18.0 Hz, $P(CH_3)_3$).

Synthesis of $Os(CO)_2(PMe_3)_2(\eta^2\text{-}CF_3C_2H)$, 3b

To a pentane solution (25ml) of $Os(CO)_4(\eta^2\text{-TFP})$ (82.5 mg, 0.208 mmol) at 0°C, trimethylphosphine (43 mL, 0.416 mmol) was added and the solution was stirred at 0°C for 16 h before it was allowed to warm to room temperature, and was maintained stirring at room temperature for 70 min. The original colorless solution changed to pale yellow. The solution was then cooled to - 78°C and the solvent was removed in vacuo at this temperature. Recrystallization from pentane at - 78°C gave 96 mg (94%) of a pale yellow powder (**3b**). Anal. Calcd. for $C_{11}H_{19}O_2P_2F_3Os$: C, 26.83; H, 3.89. Found: C, 27.19; H, 3.83. MS (70 ev, 220°C, m/e): M^+ - n CO, n = 0 - 2.

IR (pentane, cm^{-1}): υ_{CO}: 1984 s, 1918 s; $\upsilon_{C\equiv C}$: 1685w, 1669w.

^{1}H NMR: 7.05 (m, $^4J_{HF}$ = 3.4 Hz, 1H), 1.33 (t, J_{HP} = 3.6 Hz, 18H).

^{31}P{^{1}H} NMR: - 43.1 (q, $^4J_{PF}$ = 4.1 Hz).

^{19}F NMR : - 53.5 (dt, $^4J_{FH}$ = 3.4 Hz, $^4J_{PF}$ = 4.1 Hz)

^{13}C{^{1}H} NMR: 189.3 (dq, $^2J_{CP}$ = 9.1 Hz, $^4J_{CF}$ = 4.5 Hz, 1 CO), 187.5 (t, $^2J_{CP}$ = 9.0 Hz, 1 CO), 17.2 (t, J_{CP} = 17.6 Hz, $P(CH_3)_3$).

Synthesis of $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CF_3C_2CF_3)$, 3c

A colorless solution of PPh_3 (87 mg, 0.332 mmol) in 14 mL CH_2Cl_2 was added via cannula into a solution of $Os(CO)_4(\eta^2\text{-HFB})$ **1b** (77 mg, 0.166 mmol) in 14 mL pentane. The mixture was stirred for 3 h at room temperature. The solvent was then removed in vacuo to give a white solid. Recrystallization from CH_2Cl_2/pentane gave **3c** as a white powder (136 mg, 88%). Anal. Calcd. for $C_{42}H_{30}O_2P_2F_6Os$: C, 54.08; H, 3.24. Found: C, 53.97; H, 2.93.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2001 s, 1935 vs; $\upsilon_{C\equiv C}$: 1731 w.

^{1}H NMR: 7.5 (m, Ph).

^{31}P{^{1}H} NMR: 8.60 (sept, $^4J_{PF}$ = 2.8 Hz).

^{19}F NMR: - 51.98 (t, $^4J_{PF}$ = 2.8 Hz).

^{13}C{^{1}H} NMR: 186.03 (t, $^2J_{PC}$ = 9.06 Hz, CO), 121.68 (q, $^1J_{CF}$ = 269.3 Hz, CF_3), 110.30 (m, CCF_3).

Synthesis of $Ru(CO)_2(PMe_3)_2(\eta^2\text{-}CF_3C_2CF_3)$, 3d

The complex $Ru(CO)_4(\eta^2\text{-HFB})$ **1a** (68 mg, 0.181 mmol) was dissolved in 20 mL pentane and PMe_3 (37.5 µl, 0.363 mmol) was added to it with syringe. The clear solution quickly turned pale yellow. The solution was stirred for 2 h. The solvent was removed in vacuo at - 78°C. The residue

was washed several times with pentane at - 78°C to give **3d** (72 mg, 84%) as a pale yellow powder. Anal. Calcd. for $C_{12}H_{18}O_2P_2F_6Ru$: C, 30.58; H, 3.85. Found: C, 30.65; H, 3.66. MS (70 ev, 220°C): M^+ - n CO, n = 0 - 2.
IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2005 m, 1940 s; $\upsilon_{C\equiv C}$: 1764 w.

^1H NMR: 1.26 (t, $^2J_{PH}$ = 3.5 Hz).

$^{31}P\{^1H\}$ NMR: - 5.9 (sept, $^4J_{PF}$ = 2.6 Hz).

^{19}F NMR: - 53.2 (t, $^4J_{PF}$ = 2.6 Hz).

$^{13}C\{^1H\}$ NMR : 203.9 (t, $^2J_{CP}$ = 11.8 Hz, CO), 125.2 (q, $^1J_{CF}$ = 266.6 Hz, CF_3), 116.5 (qq, $^2J_{CF}$ = 43.3 Hz, $^3J_{CF}$ = 7.0 Hz, CCF_3), 18.2 (t, $^2J_{CP}$ = 15.5 Hz, $P(CH_3)_3$).

Synthesis of $Ru(CO)_2(PPh_3)_2(\eta^2\text{-}CF_3C_2CF_3)$, 3e

A colorless solution of $Ru(CO)_4(\eta^2\text{-HFB})$ **1a** (50 mg, 0.133 mmol) in 5 mL CH_2Cl_2 was transferred via a cannula into a solution of PPh_3 (70 mg, 0.266 mmol) in 5 mL CH_2Cl_2 at 0°C. The mixture was stirred and allowed to slowly warm up to room temperature over 2 h. The CH_2Cl_2 was removed in vacuo to give a white solid which was recrystallized from CH_2Cl_2/pentane to yield 108 mg (96%) of **3e** as a white powder. Anal. Calcd. for $C_{42}H_{30}O_2P_2F_6Ru.CH_2Cl_2$: C, 55.62; H, 3.47. Found: C, 55.38; H, 3.11.
IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2010 m, 1949 s; $\upsilon_{C\equiv C}$: 1752 w.

^1H NMR (- 60°C): 7.4 (m, Ph).

$^{31}P\{^1H\}$ NMR (- 60°C): 41.1 (br s).

^{19}F NMR (- 60°C): - 51.0 (t, $^4J_{PF}$ = 2.3 Hz).

$^{13}C\{^1H\}$ NMR (- 60°C): 203.5 (t, $^2J_{CP}$ = 12 Hz, CO).

Reaction of $Os(CO)_4(\eta^2-C_2Me_2)$ with PMe_3:

Trimethylphosphine (11 µL, 0.106 mmol) was added to a colorless solution of $Os(CO)_4(\eta^2-C_2Me_2)$ (35 mg, 0.0983 mmol) in 20 mL pentane at - 78°C. The solution was allowed to warm to room temperature, during which time the color of the solution changed to yellow. The solvent was then removed in vacuo. Recrystallization from CH_2Cl_2/pentane gave several products as pale yellow solids. Further isolation of these products was not successful.

Reaction of $Os(CO)_4(\eta^2-C_2H_2)$ with excess PMe_3:

Trimethylphosphine (3.1 mL, 29.9 mmol) was added to a colorless solution of $Os(CO)_4(\eta^2-C_2H_2)$ (100 mg, 0.305 mmol) in 35 mL pentane at 0°C. The solution gradually turned yellow over 65 h at 0°C. The yellow solution was then cooled to - 78°C and the solvent was removed at this temperature to give a mixture of compounds $Os(CO)_2(PMe_3)_2(\eta^2-C_2H_2)$ **3f**, trans-$Os(CO)_2(PMe_3)_2\{\eta^2-C_2H_2C(O)\}$ **4a**, and cis-$Os(CO)_2(PMe_3)_2\{\eta^2-C_2H_2C(O)\}$ **4b**. Sublimation in a closed vacuum system from - 78°C to ambient temperature gave 41 mg (32%) of **3f** as a white solid. After sublimation the residue was separated by column chromatography employing silica gel and 70% THF/hexane as an eluting mixture. The first fraction proved to be **4b** (19 mg, 14%) as a yellow solid, the second fraction was **4a** (36 mg, 26%) as a yellow solid as well. The elemental analysis and spectroscopic data for these compounds are listed below.

3f:

Anal. Calcd. for $C_{10}H_{20}O_2P_2Os$: C, 28.30; H, 4.75. Found: C, 28.58; H, 3.96.

MS (FAB): M^+ - nCO, n = 0-2.

IR (pentane, cm^{-1}): υ_{CO}: 1962 m, 1897 s.

^{1}H NMR (- 10°C): 1.23 (t, J_{HP} = 3.66 Hz, 2PMe$_3$), 6.30 (t, $^3J_{HP}$ = 2.92 Hz, 2H).

^{31}P{^{1}H} NMR (- 10°C): - 44. 64 (s).

^{13}C{^{1}H} NMR (- 20°C): 192.5 (t, $^2J_{CP}$ = 8.9 Hz, CO), 94.5 (t, $^2J_{CP}$ = 2.6 Hz, C_2H_2), 16.9 (t, J_{CP} = 17.7 Hz, P(CH$_3$)$_3$).

4a:

Anal. Calcd. for $C_{11}H_{20}O_3P_2Os$: C, 29.20; H, 4.46. Found: C, 29.49; H, 4.41

MS (EI): M$^+$ - nCO, n = 0-2.

IR (pentane, cm^{-1}): υ_{CO}: 1996 m, 1932 s; υ_{acyl}: 1652w.

^{1}H NMR: 8.65 (dt, $^2J_{HH}$ = 6.87 Hz, $^3J_{PH}$ = 1.45 Hz, CH$_\beta$), 8.41 (dt, $^2J_{HH}$ = 6.87 Hz, $^3J_{PH}$ = 4.48 Hz, CH$_\alpha$), 1.59 (dd, J_{PH} = 3.98 Hz, 2 PMe$_3$).

^{31}P{^{1}H} NMR: - 41.49 (s)

^{13}C{^{1}H} NMR: 213.4 (t, $^2J_{CP}$ = 10.80 Hz, acyl), 186.5 (t, $^2J_{CP}$ = 7.3 Hz, 1CO), 185.3 (t, $^2J_{CP}$ = 6.0 Hz, 1 CO), 166.7 (t, $^2J_{CP}$ = 7.1 Hz, Os-C(O)-C$_\alpha$H), 159.9 (t, $^2J_{CP}$ = 12.5 Hz, Os-C$_\beta$H), 18.2 (t, J_{CP} = 18.2 Hz, P(CH$_3$)$_3$).

4b:

Anal. Calcd. for $C_{11}H_{20}O_3P_2Os$: C, 29.20; H, 4.46. Found: C, 29.71; H, 3.98.

IR (pentane, cm^{-1}): υ_{CO}: 2010 s, 1938 vs; υ_{acyl}: 1649 w.

^{1}H NMR: 8.83 (ddd, $^3J_{HH}$ = 6.2 Hz, $^3J_{PaH}$ = 0.7 Hz, $^3J_{PbH}$ = 3.1 Hz, H$_\beta$), 8.34 (ddd, $^3J_{HH}$ = 6.2 Hz, $^4J_{PaH}$ = 4.2 Hz, $^4J_{PbH}$ = 8.7 Hz, H$_\alpha$), 1.68 (d, $^2J_{PaH}$ = 9.2 Hz, P$_b$Me$_3$), 1.48 (d, $^2J_{PbH}$ = 9.0 Hz, P$_a$Me$_3$)

^{31}P{^{1}H} NMR: Pa: - 44.4 (d, $^2J_{PP}$ = 21 Hz), Pb: - 50.1 (d, $^2J_{PP}$ = 21 Hz).

^{13}C{^{1}H} NMR (- 10°C): 207.8 (dd, $^2J_{CP}$ = 11.4 Hz), $^2J_{CP}$ = 3.7 Hz, acyl), 188.3 (dd, $^2J_{CP}$ = 89.7 Hz, $^2J_{CP}$ = 7.7 Hz, 1CO), 186.5 (dd, $^2J_{CP}$ = 9.7 Hz, $^2J_{CP}$ = 4.9 Hz, 1CO), 166.3 (d, $^3J_{CP}$ = 6.5 Hz, Os-C(O)-C$_\alpha$H), 154.7 (dd, $^2J_{CPb}$= 43.8 Hz, $^2J_{CPa}$ = 13.3 Hz, Os-C$_\beta$H), 20.0 (d, $^1J_{CP}$ = 32.6 Hz, P(CH$_3$)$_3$), 16.0 (d, $^1J_{CP}$ = 34.0 Hz, P(CH$_3$)$_3$).

Synthesis of $Os(CO)_3\{P(^tBu)_3\}\{\eta^2\text{-}C(O)C_2H_2C(O)\}$, 5a

Tri-tert-butylphosphine (36 µl, 0.153 mmol) was added to a colorless solution of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ (50 mg, 0.153 mmol) in 12 mL pentane at 0°C. The solution was stirred at this temperature for 2.5 h. The solution gradually changed to yellow suspension. The supernatant was removed via a cannula at 0°C. The residue was washed with pentane at this temperature to afford **5a** (27 mg, 42 %) as a yellow powder. Pure compound **5a** for elemental analysis was obtained from the reaction under CO atmosphere. Anal. Calcd. for $C_{19}H_{29}O_5OsP$: C, 40.85; H, 5.23. Found: C, 40.32; H, 4.79.

IR (pentane, cm^{-1}): υ_{CO}: 2081 s, 2016 s, 1980vs; υ_{acyl}: 1614 w.

^1H NMR : 6.86 (d, $^4J_{PH}$ = 0.61 Hz, 2 H), 1.45 (d, $^3J_{PH}$ = 12.5 Hz, 27 H).

$^{31}P\{^1H\}$ NMR : 55.0 (s).

$^{13}C\{^1H\}$ NMR: 246.6 (d, $^2J_{CP}$ = 7.9 Hz, 2(acyl)), 179.4 (d, $^2J_{CP}$ = 10.2 Hz, 2CO), 173.5 (d, $^2J_{CP}$ = 115 Hz, 1CO), 164.3 (s, C_2H_2), 43.7 (d, $^2J_{CP}$ = 11.3 Hz, $P(CMe_3)_3$), 32.3 (br, $P(CMe_3)_3$).

Synthesis of $Os(CO)_3\{P(^tBu)_3\}\{\eta^2\text{-}C(O)C(Me)C(Me)C(O)\}$, 5b

Tri-tert-butylphosphine (33 µl, 0.140 mmol) was added into a colorless solution of $Os(CO)_4(MeC_2Me)$ (50 mg, 0.140 mmol) in 20 mL pentane at - 78°C. The solution was stirred and slowly allowed to warm to ambient temperature over 8 h. The color of the solution gradually changed and a yellow, then orange suspension formed. The mixture was cooled to -78°C and the solvent was removed in vacuo at this temperature. The residue was recrystallized from CH_2Cl_2/penatene at - 20°C to give **5b** (24 mg, 29 %) of a light orange crystalline solid. Anal. Calcd. for $C_{21}H_{33}O_5OsP$: C, 42.99; H, 5.67. Found: C, 40.98; H, 6.08. MS (FAB): M^+ - n CO, n = 0 - 3.

IR (pentane, cm^{-1}): ν_{CO}: 2078 s, 2012s, 1994 vs; ν_{acyl}: 1608w.

^{1}H NMR: 1.81 (s, 6H), 1.42 (d, $^{3}J_{PH}$ = 12.6 Hz, 27H).

^{31}P{^{1}H} NMR: 54.1 (s).

^{13}C{^{1}H} NMR: 242.9 (d, $^{2}J_{CP}$ = 7.8 Hz, 2CO$_{acyl}$), 179.8 (d, $^{2}J_{CP}$ = 10.6 Hz, 2C$_{eq}$O), 173.2 (d, $^{2}J_{CP}$ = 68.8 Hz, 1C$_{ax}$O), 168. 2 (s, -(Me)C=C(Me)-), 43.4 (d, $^{1}J_{CP}$ = 10.6 Hz, P(CMe$_3$)$_3$), 33.1 {s, P(C*Me*$_3$)$_3$), 10.8 (s, C(O)C(*Me*)=).

^{13}C NMR: 242.9 (d, $^{2}J_{CP}$ = 7.8 Hz, 2CO$_{acyl}$), 179.8 (d, $^{2}J_{CP}$ = 10.6 Hz, 2C$_{eq}$O), 173.2 (d, $^{2}J_{CP}$ = 68.8 Hz, 1C$_{ax}$O), 168.2 (m), 33.1 (dq, $^{1}J_{CP}$ = 10.6 Hz, $^{1}J_{CH}$ = 127.6 Hz), 10.8 (q, $^{1}J_{CH}$ = 128.1 Hz).

Synthesis of Os(CO)$_2$(PMe$_3$)$_2$(H)(C$_2$H), 6

A colorless solution of compound **3f** (15 mg, 0.353 mmol) in 5 mL CH$_2$Cl$_2$ was allowed to warm to room temperature. After stirring for 2 h, the solvent was stripped off in vacuo. Recrystallization from pentane gave **6** (9 mg, 60%) as a white powder. Anal. Calcd. for $C_{10}H_{20}O_2P_2Os$: C, 28.30; H, 4.75. Found: C, 28.33; H, 4.55.

IR (pentane, cm^{-1}): ν_{CO}: 2023 m, 1958 s.

^{1}H NMR: - 7.70 (t, $^{2}J_{PH}$ = 22.2 Hz, 1H), 1.51 (t, $^{4}J_{PH}$ = 4.1 Hz, C$_2$H), 1.75 (t, J_{PH} = 4.1 Hz, 2 PMe$_3$).

^{31}P{^{1}H} NMR: - 47. 0 (s).

^{13}C{^{1}H} NMR: 182.8 (t, $^{2}J_{CP}$ = 7.7 Hz, 1CO), 181.1 (t, $^{2}J_{CP}$ = 7.7 Hz, 1CO), 93.4 (t, $^{3}J_{CP}$ = 2.7 Hz, CCH), 87.0 (t, $^{2}J_{CP}$ = 17.2 Hz, CCH), 21.0 (t, J_{CP} = 19.0 Hz, P(CH$_3$)$_3$).

Synthesis of Os$_2$(CO)$_5$(PMe$_3$)$_2${μ-η^1: η^2-C$_2$H$_2$C(O)C$_2$H$_2$}, 7

Trimethylphosphine (28.9 mL, 0.279 mmol) was added to a solution of Os(CO)$_4$(η^2-C$_2$H$_2$) (91.7 mg, 0.279 mmol) in 35 mL pentane at 0°C. The colorless solution was stirred at 0°C for 3 h, its color gradually turned yellow. The yellow solution was then allowed to warm to room temperature, resulting in the formation of an orange precipitate. The mixture was stirred for an additional 12 h. The solvent was removed in vacuo. The residue was washed by adding 5 mL hexane at room temperature and stirring for a few minutes, followed by cooling to - 78°C. The supernatant was then removed by syringe. After this process was repeated three times, the resulting yellow powder was dried under vacuum . The yield of **7** was 62 mg (59%). Anal. Calcd for $C_{16}H_{22}O_6P_2Os_2$: C, 25.53; H, 2.95. Found: C, 25.09; H, 2.74. MS (70ev, 200°C, m/e): M^+ - n CO, n = 0-5.

IR (pentane, cm^{-1}): υ_{CO}: 2052m, 2022m, 1990vs, 1978s, 1936m; υ_{acyl}: 1605w.

IR (pentane, cm^{-1}, with ^{13}CO enriched product): υ_{CO}: 2006m, 1973m, 1944vs, 1934s, 1904m; υ_{acyl}: 1570w.

^1H NMR: H'_β: 9.30 (dd, $^3J_{H'_\alpha H'_\beta}$ = 12.60 Hz, $^2J_{PaH'_\beta}$ = 5.36 Hz), H_β: 8.79 (d, $^3J_{H_\alpha H_\beta}$ = 9.32 Hz), H'_α: 6.25 (ddd, $^3J_{H'_\alpha H'_\beta}$ = 12.60 Hz, $^4J_{P_aH'_\alpha}$ = 2.24 Hz, $^3J_{H_\alpha H'_\alpha}$ = 1.00 Hz), H_α: 4.65 (ddd, $^3J_{H_\alpha H_\beta}$ = 9.32 Hz, $^3J_{P_bH_\alpha}$ = 5.96 Hz, $^3J_{H_\alpha H'_\alpha}$ = 1.00 Hz), H_{P_b}: 1.88 (d, $^2J_{P_bH}$ = 10.60 Hz, 9H), H_{P_a}: 1.83 (d, $^2J_{P_aH}$ = 10.72 Hz, 9H).

$^{31}P\{^1H\}$ NMR: P_a: - 31.2 (s), P_b: - 51.1 (s).

$^{13}C\{^1H\}$ NMR: 202.0 (s, acyl), 191.1 (dd, $^3J_{CPa}$ = 4.8 Hz, $^2J_{CP_b}$ = 6.4 Hz, $1C_{c/d}O$), 189.5 (d, $^2J_{CP_a}$ = 6.4 Hz, $1C_{a/b}O$), 188.4 (d, $^2J_{CP_b}$ = 6.3 Hz, $1C_{c/d}O$), 183.8 (d, $^2J_{CP_a}$ = 6.3 Hz, $1C_{a/b}O$), 180.5 (s, $1C_eO$), 173.8 (d, $^2J_{CP_a}$ = 8.3 Hz, CH'_β), 134.9 (s, CH_β), 131.9 (s, CH'_α), 64.9 (c, CH_α), 22.6 (d, $^1J_{CP_a}$ = 39.6 Hz, P_aMe_3), 19.5 (d, $^1J_{CP_b}$ = 37.9 Hz, P_bMe_3).

$^{13}C\{^1H\}$ NMR (with ^{13}CO enriched product): 202.0 (s, acyl), 191.1 (ddd, $^3J_{CP_a}$ = 4.8 Hz, $^2J_{CP_b}$ = 6.4 Hz, $^2J_{CC}$ = 34.5 Hz,$1C_{c/d}O$), 189.5 (d, $^2J_{CP_a}$ = 6.4 Hz,

$1C_{a/b}O$), 188.4 (dd, $^2J_{CP_b}$ = 6.3 Hz, $^2J_{CC}$ = 34.5 Hz, $1C_{c/d}O$), 183.8 (d, $^2J_{CP_a}$ = 6.3 Hz, $1C_{a/b}O$), 180.5 (s, $1C_eO$), 173.8 (dd, $^2J_{CP_a}$ = 8.3 Hz, $^2J_{CC}$ = 17.7 Hz, CH'_β), 134.9 (d, $^2J_{CC}$ = 21.5 Hz, CH_β), 131.9 (d, $^2J_{CC}$ = 55.8 Hz, CH'_α), 64.9 (d, $^2J_{CC}$ = 49.7 Hz, CH_α), 22.6 (d, $^1J_{CP_a}$ = 39.6 Hz, P_aMe_3), 19.5 (d, $^1J_{CP_b}$ = 37.9 Hz, P_bMe_3).

^{13}C NMR: 173.8 (dd, $^2J_{CP_a}$ = 8.3 Hz, $^1J_{CH}$ = 132 Hz, CH'_β), 134.9 (d, $^1J_{CH}$ = 141.7 Hz, CH_β), 131.9 (d, $^1J_{CH}$ = 155.31 Hz, CH'_α), 64.9 (d, $^1J_{CH}$ = 151.9 Hz, CH_α), 22.6 (dm, $^1J_{CP_a}$ = 39.6 Hz, P_aMe_3), 19.5 (dm, $^1J_{CP_b}$ = 37.9 Hz, P_bMe_3).

2.5. References

(1) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983,** *83,* 203.

(2) Schore, N. E. *Chem. Rev.* **1988,** *88,* 1081.

(3) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation. Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991.

(4) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis;* 2 ed.; Wiley-Interscience: NY, 1992, pp 191-216.

(5) Hubel, W.; Braye, E. H.; Clauss, A.; Weiss, E.; Kruerke, D.; Brown, D. A.; King, G. S. D.; Hoogzand, C. *J. Inorg. Nucl. Chem.* **1959,** *9,* 204.

(6) Hubel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959,** *10,* 250.

(7) Hubel, W. In *Organic Synthesis via Metal Carbonyls;* I. Wender and P. Pino, Ed.; Wiley: New York, 1968; Vol. 1; pp 273-371.

(8) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980,** *102,* 1532.

(9) Templeton, J. L.; Herrick, R. S.; Morrow, J. R. *Organometallics* **1984,** *3,* 535.

(10) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1987,** *109,* 1401.

(11) Templeton, J. L. *Adv. Organomet. Chem.* **1989,** *29,* 1.

(12) Alt, H. G. *J. Organomet. Chem.* **1985,** *288,* 149.

(13) Alt, H. G.; Han, J. S.; Rogers, R. D.; Thewalt, U. *J. Organomet. Chem.* **1993,** *459,* 209.

(14) Davidson, J. L.; Vasapollo, G. *Polyhedron* **1983,** *2,* 305.

(15) Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1986,** 2423.

(16) Lee, W.-S.; Brintzinger, H. H. *J. Organomet. Chem.* **1977,** *127,* 93.

(17) Pannell, K. H.; Crawford, G. M. *J. Coord. Chem.* **1973,** *2,* 251.

(18) Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* **1987,** *6,* 1918.

(19) Gagne, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561.

(20) Burn, M. J.; Kiel, G.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850.

(21) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

(22) Anderson, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 446.

(23) Pearson, J. M.; Jordan, R. B.; Takats, J., Unpublished Work.

(24) Angelici, R. J. *Organomet. Chem. Rev.* **1968**, *3*, 173.

(25) Basolo, F. *Inorg. Chim. Acta.* **1981**, *50*, 65.

(26) Atwood, J. D.; Wovkulich, M. J.; Sonnenberger, D. C. *Acc. Chem. Res.* **1983**, *16*, 350.

(27) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155.

(28) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

(29) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

(30) Zhang, Z. S.; Jordan, R. B.; Takats, J., Personal Communication.

(31) Kiel, G.; Takats, J., Unpublished Work.

(32) Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. (A)* **1970**, 2981.

(33) Wong, W.; Singer, S. J.; Pitts, W. D.; Watkins, S. F.; Baddley, W. H. *J. Chem. Soc., Chem. Commun.* **1972**, 672.

(34) Corrigan, P. A.; Dickson, R. S. *Aust. J. Chem.* **1979**, *32*, 2147.

(35) Padolik, L. L.; Callucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 9986.

(36) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry;* 5th ed.; A Wiley-Interscience Publication: New York, 1988, pp 1034-1038.

(37) Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley-Interscience, John Wiley & Sons, Inc.: New York, 1972, pp 28-29.

(38) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975,** *14,* 365.

(39) Marinell, G.; Streib, W. E.; Huffman, J. C.; Caulton, K. G.; Gagne, M. R.; Takats, J.; Dartiguenave, M.; Chardon, C.; Jackson, S. A.; Eisenstein, O. *Polyhedron* **1990,** *9,* 1867.

(40) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Oro, L. A. *J. Organomet. Chem.* **1994,** *468,* 223.

(41) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975,** *97,* 3380.

(42) Cotton, E. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974,** *96,* 3438.

(43) Cobbledick, R. E.; Einstein, F. W.; Pomeroy, R. K. *J. Organomet. Chem.* **1980,** *195,* 77.

(44) Cowley, A. H.; Davis, R. E.; Remanda, K. *Inorg. Chem.* **1981,** *20,* 2146.

(45) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *J. Organomet. Chem.* **1990,** *391,* 367.

(46) Glaser, R.; Yoo, Y.; Chen, G. S.; Barnes, C. L. *Organometallics* **1994,** *13,* 2578.

(47) Leplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1968,** *7,* 1290.

(48) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987, pp 355-394.

(49) Blomberg, M. R. A.; Karlsson, C. A. M.; Siegbahn, P. E. M. *J. Phys. Chem.* **1993,** *97,* 9341.

(50) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967,** *10,* 101.

(51) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981,** *103,* 4410.

(52) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1988,** *110,* 3728.

(53) Andersen, J.; Moss, J. R. *Organometallics* **1994,** *13,* 5013.

(54) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986,** *303,* 221.

(55) Walker, H. W.; Ford, P. C. *J. Organomet. Chem.* **1981**, *214*, C43.

(56) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta.* **1985**, *68*, 1461.

(57) Alonso, F. J. G.; Hohn, A.; Wolf, J.; Werner, H. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 406.

(58) Hohn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852.

(59) Werner, H.; Baum, M.; Schneider, D.; Windmuller, B. *Organometallics* **1994**, *13*, 1089.

(60) Loots, M. J.; Weingarten, L. R.; Levin, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 4571.

(61) Aime, S.; Gobetto, R.; Nicola, G.; Osella, D.; Milone, L.; Rosenberg, E. *Organometallics* **1986**, *5*, 1829.

(62) Kiel, G.; Takats, J. *Organometallics* **1989**, *8*, 839.

(63) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

(64) Takats, J.; Washington, J.; Santarsiero, B. *Organometallics* **1994**, *13*, 1078.

(65) Washington, J. Ph. D. Thesis, University of Alberta, 1994.

(66) Mirza, M. A.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1994**, *13*, 3063.

(67) Tachikawa, M.; Richter, S. I.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *128*, C9.

(68) Pearson, A. J.; Shively, R. J. *Organometallics* **1994**, *13*, 578.

(69) Hubel, W. In ; I. Wender and P. Pino, Ed.; Interscience Publishers: New York, 1968; Vol. 1; pp 273-342.

(70) Pino, P.; Braca, G. In *Organic Synthesis via Metal Carbonyls*; I. Wender and P. Pino, Ed.; Wiley: New York, 1977; Vol. 2; pp 419 - 516.

(71) Bruce, M. I.; Jensen, C. M.; Jones, N. L. *Inorg. Synth.* **1989**, *26*, 259.

(72) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1975**, 1876.

(73) Rushman, P.; van Buuren, G. N.; Shiralian, M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 693.

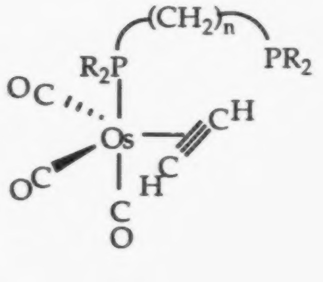
(74) Washington, J.; McDonald, R.; Takats, J.; Menashe, N.; Reshef, D.; Shvo, Y. *Organometallics* **1995**, *14*, 3996.

Chapter 3

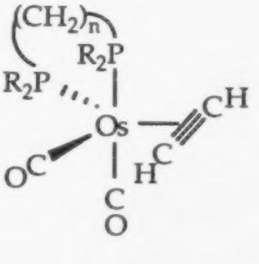
Reactions of $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) Complexes with Diphosphines

3.1. Introduction

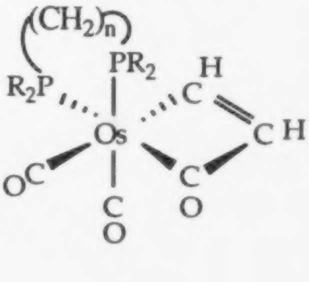
In the previous chapter, the reactions of $M(CO)_4(\eta^2\text{-alkyne})$ complexes with monophosphines were described. In general, the reactions with one equivalent of PR_3 (R = Me, Ph) gave the corresponding CO substitution products. When two equivalents or an excess of PR_3 were used, two types of products were obtained. With electron-poor alkynes, such as $CF_3C_2CF_3$, a second CO was replaced also. In the case of electron rich alkynes, such as C_2H_2, CO insertion products were obtained. In order to expand the scope of this chemistry, the reaction with diphosphines $R_2P(CH_2)_nPR_2$ (n = 1, R = Ph, dppm, R = Me, dmpm; n = 2, R = Ph, dppe, R = Me, dmpe) was undertaken. Based on the previous precedents described in Chapter 2, three types of products (H, I, and J) may be anticipated. Each type offers attractive attributes for further elaboration.



H



I



J

It is well documented that the dppm ligand has a strong tendency to bridge dinuclear centers and is widely used for the synthesis of dinuclear complexes.[1-5] In addition, the presence of an alkyne ligand in species **H** and **I** provides the possibility for further condensation reactions. In the case of species **J**, the metallacyclobutenone may undergo ring expansion. In this chapter the results of the reactions of $M(CO)_4(\eta^2\text{-alkyne})$ compounds with diphosphines are reported.

3.2. Results and Discussion

3.2.1. Reaction of $Ru(CO)_4(\eta^2\text{-}F_3CC_2CF_3)$ with dppm and dmpm

$Ru(CO)_4(\eta^2\text{-HFB})$ (**1c**) reacts readily with dppm or dmpm to give a single product in each case in good yield (eq. 3.1).

$$\mathbf{1c} \quad + \quad R_2PCH_2PR_2 \xrightarrow[-\,5^{\circ}C \,\rightarrow\, r.\,t.]{CH_2Cl_2} \text{"}Ru(CO)_3(R_2PCH_2PR_2)(HFB)\text{"} \quad (3.1)$$

R = Ph, 74%, **8a**; Me, 70%, **8b**.

The mass spectrum of **8a** showed a parent molecular ion at m/e 732 with the expected isotope pattern, followed by loss of three carbonyls. In conjunction with elemental analysis, complex **8a** can thus be formulated as "$Ru(CO)_3(Ph_2PCH_2PPh_2)(HFB)$". The IR spectrum showed three terminal carbonyl stretching bands at 2085 (s), 2028 (m), and 2000 (s) cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum showed two distinct phosphine resonances at δ 32.9 and 47.7. The ^{19}F NMR spectrum showed two resonances at δ - 43.3 and - 48.8. Selective ^{31}P decoupling experiments clearly showed that the phosphine at δ 47.7 is not only coupled to the other phosphine at δ 32.9 but is also coupled to the fluorines of one of the CF_3 groups. The $^{13}C\{^1H\}$ NMR spectrum obtained from a ^{13}CO enriched material showed three terminal carbonyls with equal intensity at δ 198.7, 195.9, and 192.2. In combination with the $^{31}P\{^1H\}$ NMR spectrum of the same enriched sample, the carbonyl at δ 192.2 is evidently coupled to the phosphine at δ 32.9 with a coupling constant of 83 Hz, indicating a *trans* relationship, whereas the remaining two carbonyls at δ 198.7 and 195.9 are coupled to the same phosphine at δ 32.9 with a coupling constant of *ca*. 10 Hz , suggesting a mutual *cis* arrangement. The important feature is that the three carbonyls are not coupled to the other phosphine at δ 47.7. Therefore, it appears that the structure of the product is similar to the axially substituted monophosphine derivative described in Chapter 2 except that one end of dppm has some unexpected interaction with one end of the HFB ligand. Finally, the ^1H NMR spectrum showed that, surprisingly, the two methylenic protons of the dppm ligand are no longer coupled to each other. One of the protons is coupled to both phosphines, as would be typically expected for dppm ligand, but the other is coupled not only to both phosphines but also to the fluorines of one of the CF_3 groups; this was confirmed by selective $^{19}F\{^1H\}$ decoupling experiments. In order to solve the puzzle, the molecular structure of this unusual compound **8a** was determined by X-ray crystallography.

Solid-State Structure of 8a. The X-ray structure of complex **8a** is shown in Figure 3.1; Table 3.1 shows selected bond distances and bond angles.

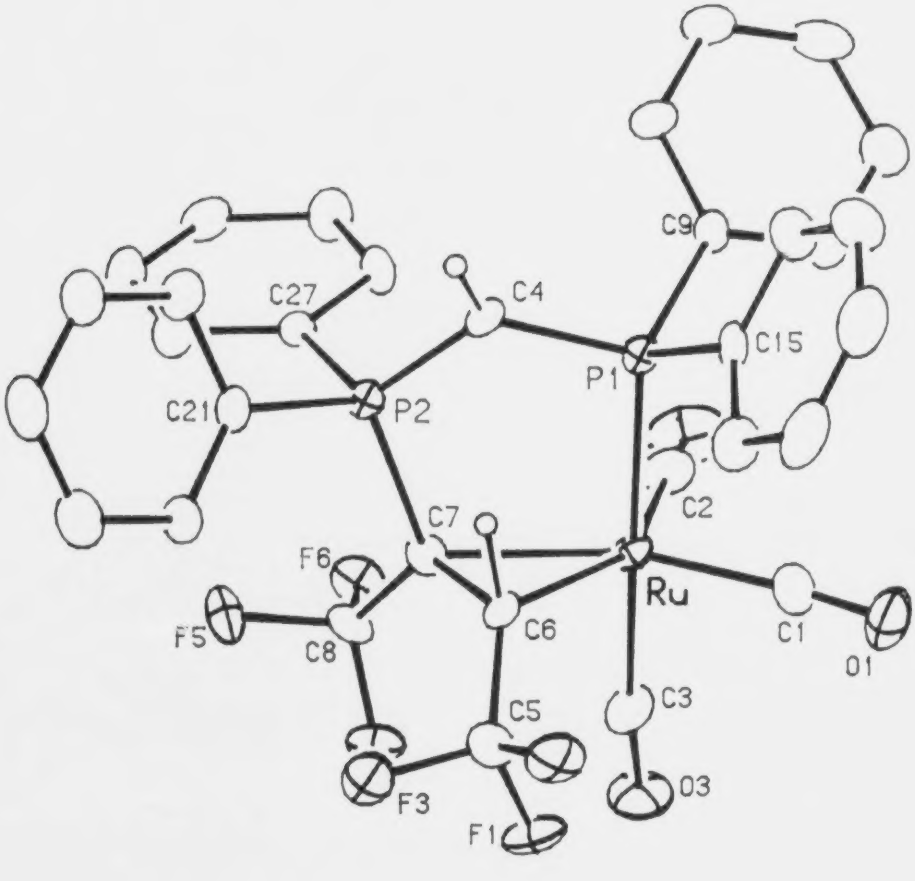
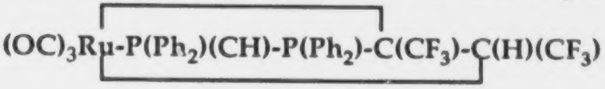

C9
C27
C4
C15
P1
C21
P2
C2
C7
F6
Ru
F5
C8
C6
C1
O1
C5
C3
F3
O3
F1

Figure 3.1: ORTEP View of

(OC)$_3$Ru-P(Ph$_2$)(CH)-P(Ph$_2$)-C(CF$_3$)-C(H)(CF$_3$) , 8a

Table 3.1: Selected Bond Distances and Angles for



$(OC)_3Ru\text{-}P(Ph_2)(CH)\text{-}P(Ph_2)\text{-}C(CF_3)\text{-}C(H)(CF_3)$, 8a

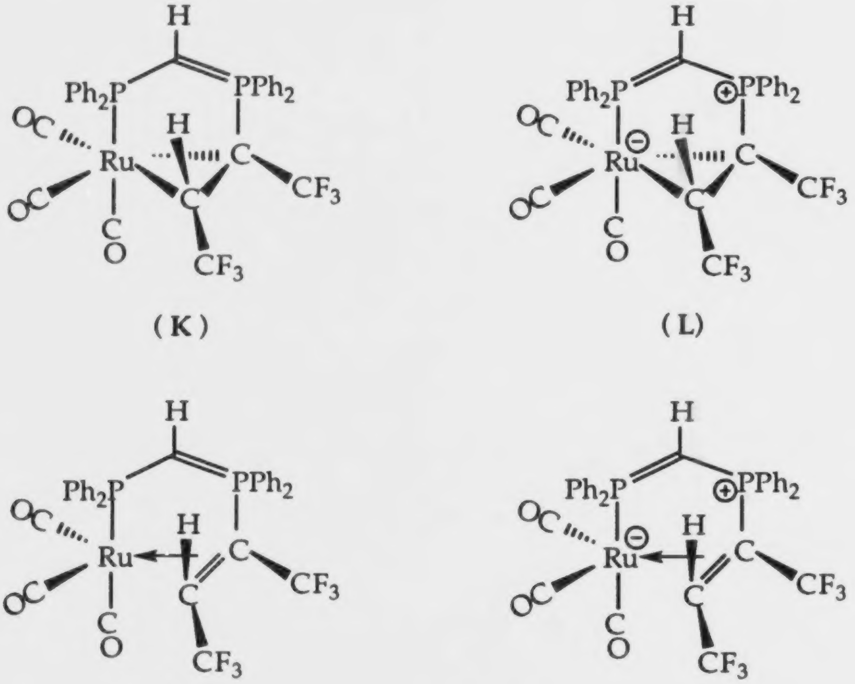
Bond Distances (Å)

Ru-C(1)	1.89(2)	Ru-C(2)	1.92(2)
Ru-C(3)	1.95(2)	Ru-C(6)	2.14(1)
Ru-C(7)	2.20(1)	Ru-P(1)	2.389(4)
P(1)-C(4)	1.72(1)	P(2)-C(4)	1.66(1)
P(2)-C(7)	1.84(1)	C(6)-C(7)	1.53(2)

Bond Angles (deg.)

P(1)-Ru-C(1)	89.2(5)	P(1)-Ru-C(2)	90.8(5)
C(1)-Ru-C(2)	102.7(7)	P(1)-Ru-C(3)	178.5(5)
C(1)-Ru-C(3)	90.2(7)	C(2)-Ru-C(3)	88.0(7)
P(1)-Ru-C(6)	86.6(3)	C(1)-Ru-C(6)	105.6(6)
C(2)-Ru-C(6)	151.5(6)	C(3)-Ru-C(6)	94.9(6)
P(1)-Ru-C(7)	88.4(3)	C(1)-Ru-C(7)	147.0(6)
C(6)-Ru-C(7)	41.4(4)	Ru-P(1)-C(4)	105.8(5)
P(1)-C(4)-P(2)	120.4(7)	C(4)-P(2)-C(7)	108.7(6)

The structure reveals that, as expected, one phosphine is coordinated to the ruthenium center, while the other phosphorus has linked with the coordinated alkyne and undergone C-H bond cleavage and hydrogen transfer to one of the alkyne carbons from the methylene of dppm. The bonding in this interesting heterobicyclic structure can be viewed as contributions from four possible resonance forms (Scheme 3.1).



(K)

(L)

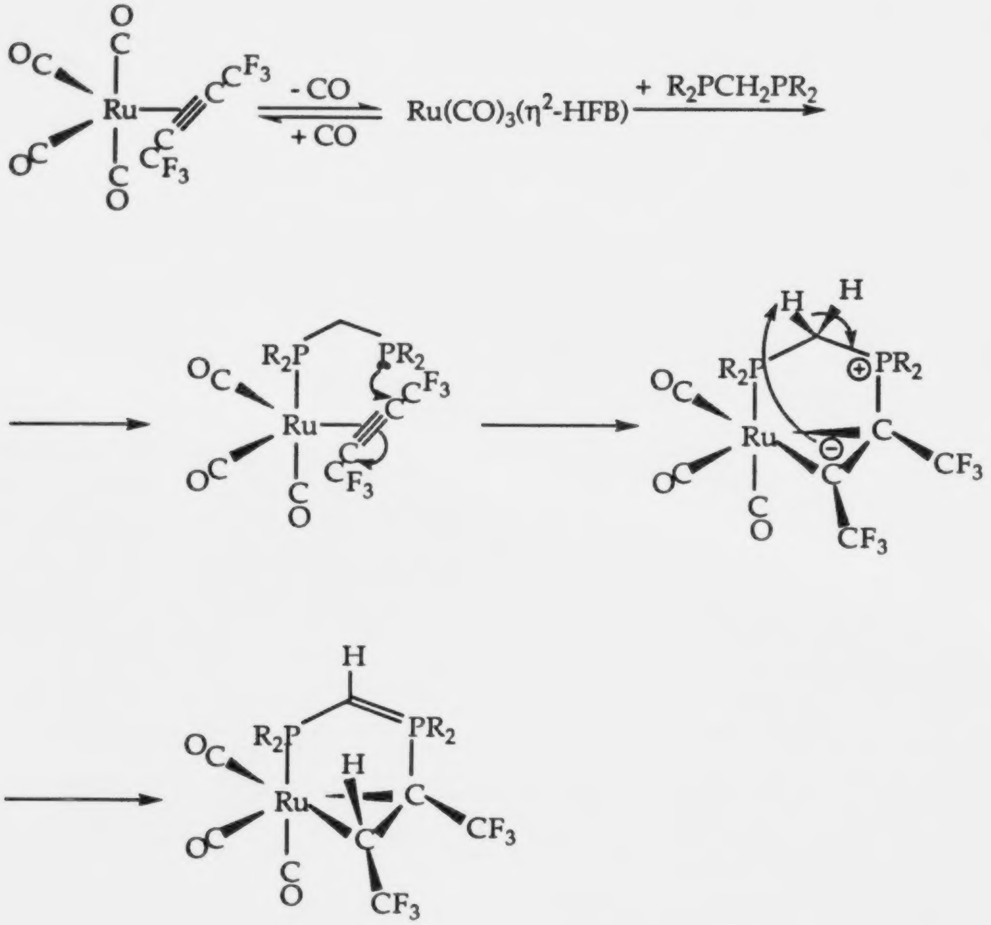
(M)

(N)

Scheme 3.1

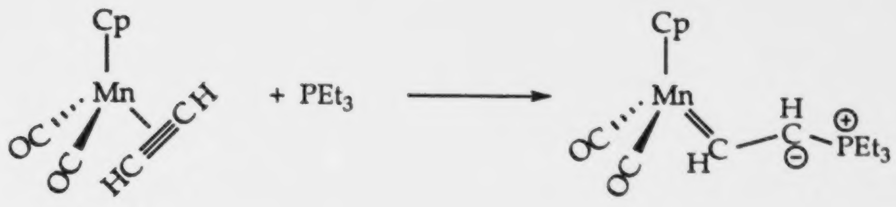
The C6-C7 bond length (1.53 (2) Å) is typical for a carbon-carbon single bond.[6] The metal-carbon distances of Ru-C(6) (2.14 (1) Å) and Ru-C(7) (2.20 (1) Å) are typical Ru-C single bonds.[7-9] Therefore, the resonance forms **M** and **N** are not likely to contribute significantly to the bonding as a shorter C-C bond distance and longer Ru-C bonds would be expected. The P1-C4 (1.72 (1) Å) and P2-C4 (1.66 (1) Å) bond distances are much shorter (by *ca* 0.1 Å) than those in dppm complexes,[1,2,5,10] but similar to those containing deprotonated dppm ligands,[11-13] thus suggest some double bond character. Since P1- C4 separation is 0.06 Å longer than the P2-C4 distance, the ylide resonance form **K** appears to make a greater contribution than the zwitterionic structure **L**. Thus the structure is best described as the ylide form **K** with some contribution from the zwitterionic form **L**. On the basis of its very similar spectroscopic features, compound **8b** is assigned an analogous structure.

Formation of 8a and 8b. In an attempt to provide an insight into the mechanism of the formation of complexes **8a** and **8b**, the reaction of $Ru(CO)_4(\eta^2\text{-}CF_3C_2CF_3)$ with dppm was monitored by low temperature ^1H, ^{19}F, and ^{31}P NMR spectroscopy. Unfortunately, no intermediate could be detected from - 80°C to room temperature; immediate product formation was seen at - 10°C. Based on the fact that the reaction of $Ru(CO)_4(\eta^2\text{-}CF_3C_2CF_3)$ with monophosphines (PR_3, R = CH_3, Ph) gives only CO substitution products with the coordinated hexafluorobutyne remaining intact, a plausible pathway for the formation of **8a** and **8b** is shown in Scheme 3.2. Initial CO dissociation, followed by coordination of one end of the dppm ligand forms an intermediate which mimics the monophosphine substitution. The dangling phosphine in this intermediate then attacks the coordinated alkyne carbon to generate a carbanion. In analogy with the deprotonation of methylene of dppm with strong bases,[14,15] this reactive carbanion readily abstracts a proton from the methylene group of the diphosphine to complete the process.



Scheme 3.2

Coupling of free or metal coordinated alkynes with a phosphine is not novel. For example, the reaction of hexafluorobutyne with phosphines is known,[16] and intermolecular addition of a phosphine to alkyne complexes to give ylide-carbene complexes[17-20] has also been observed (eq. 3.2).

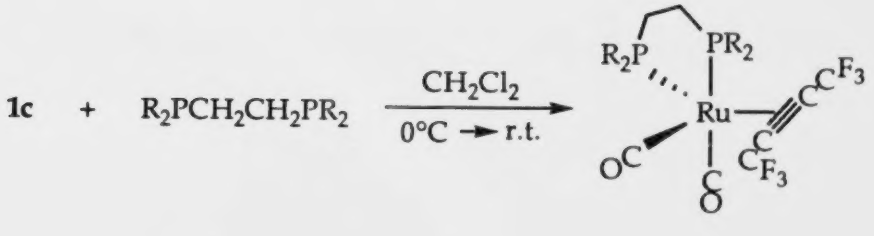


(3.2)

Recently Richmond described an intramolecular phosphine-alkyne coupling in a dicobalt system.[21,22] However, the present case appears to be the first example of intramolecular phosphine attack of a coordinated alkyne unit in a mononuclear complex. In hindsight, it is not that surprising that the reaction is observed with the highly electron deficient hexafluorobutyne ligand. Nevertheless, the facility of the deprotonation step is noteworthy. The formation of single product and the position of the hydrogen atom, syn to the methylene carbon, is consistent with an intramolecular hydrogen migration step.

3.2.2. Reaction of Ru(CO)$_4$(η^2-HFB) with dppe and dmpe.

In contrast to dppm, the reaction of Ru(CO)$_4$(η^2-HFB) (**1c**) with dppe or dmpe proceeded by simple substitution of two CO ligands and gave compounds **9a** and **9b** in moderate yields (eq. 3.3).

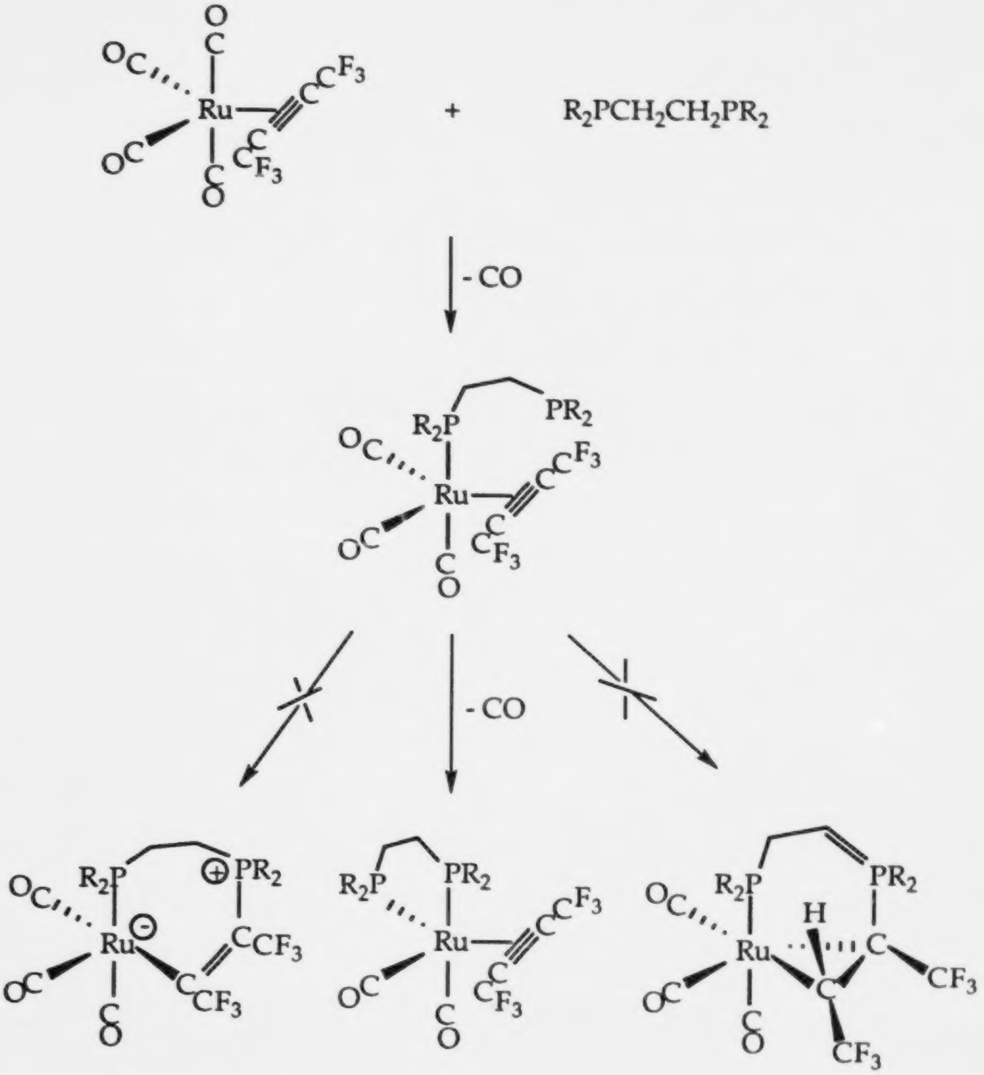


(3.3)

R = Ph, 64%, **9a**; Me, 60%, **9b**.

The IR spectrum of complex **9a** showed two carbonyl bands at 2027 and 1961 cm^{-1}, as well as an alkyne carbon-carbon stretch at 1772 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum showed two carbonyl signals with equal intensity at δ 203.8 and 195.6. The resonance at δ 195.6 appeared as a doublet of doublets with coupling to both phosphines with 118.2 Hz and 5.0 Hz, respectively. The large coupling constant indicates a *trans* arrangement between the carbonyl and the phosphine. The $^{31}P\{^1H\}$ NMR spectrum displayed two resonances at δ 65.3 and 54.4. Compared to the ^{31}P chemical shift of free dppe at δ - 12.5,[23] the large downfield shift indicates that a five-membere chelating ring has formed upon coordination of dppe.[24,25] The spectroscopic data are consistent with the structure shown in eq. 3.3. The IR, ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^{19}F NMR spectra of complex **9b** are very similar and therefore an analogous structure is assigned to it.

It is well known that the reactivity of diphosphines depends on the length of their hydrocarbon backbones.[1,2] Due to its preference to form five-membered rings, dppm and dmpm are excellent bridging ligands for the preparation of dinuclear complexes, whereas dppe and dmpe behave as classical chelating ligands and form mononuclear compounds. Indeed, the reaction of $Ru(CO)_4(\eta^2\text{-HFB})$ with dppe or dmpe results in the substitution of two CO ligands. A simple reaction sequence for the formation of compounds **9a** and **9b** is shown in Scheme 3.3.



9a, 9b

Scheme 3.3

After initial CO displacement by one end of a diphosphine, the substitution of a second CO by the dangling phosphine generates complexes **9a** and **9b**. Again, the facile substitution of CO is ascribed to the formation of an intermediate stabilized by a four-electron alkyne donor. It is interesting to note the different outcomes between substitution reactions which give **9a** and **9a** and the phosphine-alkyne coupling reactions which generate **8a** and **8b**. Note that, for both types of reactions, the first step is the same CO substitution by one end of the diphosphine. Although it is known that the dangling end of a diphosphine is less basic than the free ligand itself,[26,27] the basicity of free $Ph_2PCH_2PPh_2$ is essentially the same as that of $Ph_2P(CH_2)_2PPh_2$; the same is true for the other pair $Me_2P(CH_2)_nPMe_2$ (n = 1, 2).[26,27] As described in Chapter 2, the reaction of $Ru(CO)_4(\eta^2\text{-HFB})$ with monophosphines (PR_3, R = Ph, CH_3) gives only substitution products, even when excess phosphine was used. Thus the distinct reactivity patterns are independent of the basicity of the dangling end of the $R_2P(CH_2)_nPR_2$ (n = 1, 2) ligand. This suggests that both the decrease in the acidity of the methylene groups in dppe and dmpe, and the formation of a seven-membered chelating ring prohibit coupling between the dangling phosphine and the coordinated alkyne with these ligands.

3.2.3. Reactions of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ (1d) with dppm

The reaction of **1d** with dppm in dichloromethane leads to the formation of two complexes, **10a** and **10b** (eq. 3.4). Formulation of **10a** and **10b** are based on elemental analyses and spectroscopic data. Both compounds have identical mass spectra; a parent molecular ion at m/e 686 with the expected isotope pattern, followed by sequential loss of two carbonyls and the $C(O)C_2H_2$ fragment. The IR spectra showed two terminal carbonyl bands (**10a**: 2009, 1948 cm^{-1}; **10b**: 2002, 1946 cm^{-1}) and one band at 1633 cm^{-1} for **10a** and at 1630 cm^{-1} for **10b**. In order to identify whether the low frequency bands are due to an acyl group or a coordinated alkyne carbon-carbon stretch, a carbon-13 labelling experiment was carried out. By employing ^{13}CO enriched starting material, $Os(^{13}CO)_4(\eta^2\text{-}C_2H_2)$, the IR bands of corresponding products **10a** and **10b** shifted to lower wave numbers (**10a**: 1962, 1905, 1595 cm^{-1}. **10b**: 1955, 1903, 1593 cm^{-1}), indicating that these bands are evidently attributable to two terminal carbonyls and one acyl group. Based on these data the two isomeric compounds are formulated as the CO inserted products, $Os(CO)_2(C(O)C_2H_2)(\eta^2\text{-}dppm)$.

$$\mathbf{1d} \quad + \quad \text{dppm} \xrightarrow[-78°C \rightarrow \text{r. t.}]{CH_2Cl_2} Os(CO)_2(COC_2H_2)(dppm) \qquad (3.4)$$

10a, 10b

Table 3.2: Selected ^1H NMR Data for 10b

Compound	H_α	H_β	$^3J_{H\text{-}H}$[a]
$\{\eta^2\text{-}C_2H_2C(O)\}Os(CO)_2(dppm)$ (**10b**)	8.05	9.17	6.0
$\{\eta^2\text{-}C_2H_2C(O)\}Os(CO)_2(PMe_3)_2$ (**4a**)	8.41	8.65	6.9
$\{\eta^2\text{-}C_2H_2C(O)\}Os(CO)_2(PMe_3)_2$ (**4b**)	8.34	8.83	6.2
$\{\eta^2\text{-}C_2H_2C(O)Os(CO)_4Ru(CO)_4$[b]	7.46	8.17	9.0

a Couplings in Hz. b[28]

The ^1H spectrum of **10b** had two multiplets integrating as one proton each in the low field region at δ 9.17 and 8.05, reminiscent of the ring protons of the C*H*C*H*C(O) group (Table 3.2). For compound **10a**, these resonances were not observed due to their overlapping with the phenyl protons. The $^{31}P\{^1H\}$ NMR showed two resonances (**10a**: - 45.6, - 50.6; **10b**: - 41.9, - 39.9) at higher field with respect to free dppm, indicating that a four-membered ring has formed.[24,25] The $^{13}C\{^1H\}$ NMR spectra displayed a similar pattern for both compounds (Figure 3.2). There are three equal intensity carbonyl resonances for each compound; one carbonyl is strongly coupled to a phosphorus {**10a**: 188.5 (94 Hz); **10b**: 188.3 (92 Hz)} indicating a *trans* orientation between that carbonyl and the phosphine. In addition, the $^{13}C\{^{1}H\}$ NMR spectrum of **10a** shows that the resonance at δ 198.5, assigned to the acyl group, is a doublet of doublets and hence it is coupled to both phosphorus atoms. The large coupling (54 Hz) is due to a *trans* arrangement. In the case of **10b**, a broad-band ^{31}P and ^{1}H decoupling experiment conducted on a ^{13}CO enriched sample clearly established that the acyl group at δ 201.4 is coupled to the equatorial carbonyl at δ186.7 with a coupling constant of 17 Hz, which is in agreement with a *trans* arrangement. Therefore, it appears that compounds **10a** and **10b** can be formulated as shown in Figure 3.2.

Solid-State Structure of 10a. To corroborate the assignments, the solid state structure of **10a** was determined by single crystal X-ray crystallography. As shown in Figure 3.3, the molecule contains an osmacyclobutenone unit, Os-C(3)-C(4)-C(5), which arises from the coupling of the coordinated acetylene and a carbonyl ligand. The geometry around Os atom is distorted octahedral. One of the axial positions is occupied by P(1) while P(2) is bent away from the equatorial plane with the P(1)-Os-P(2) angle of 70.6 (1)°. In addition, the P(1)-Os-C(2) angle of 172.5 (5) is somewhat less than 180° (Table 3.3). The Os-C(3) (2.13 (2) Å) and Os-C(5) (2.11 (1) Å) bond distances are representative of normal osmium carbon single bonds.[29] As well, the C(4)-C(5) bond distance of 1.35 (2) Å and the C(3)-C(4) bond length of 1.49 (2) Å are in the typical range of C-C double

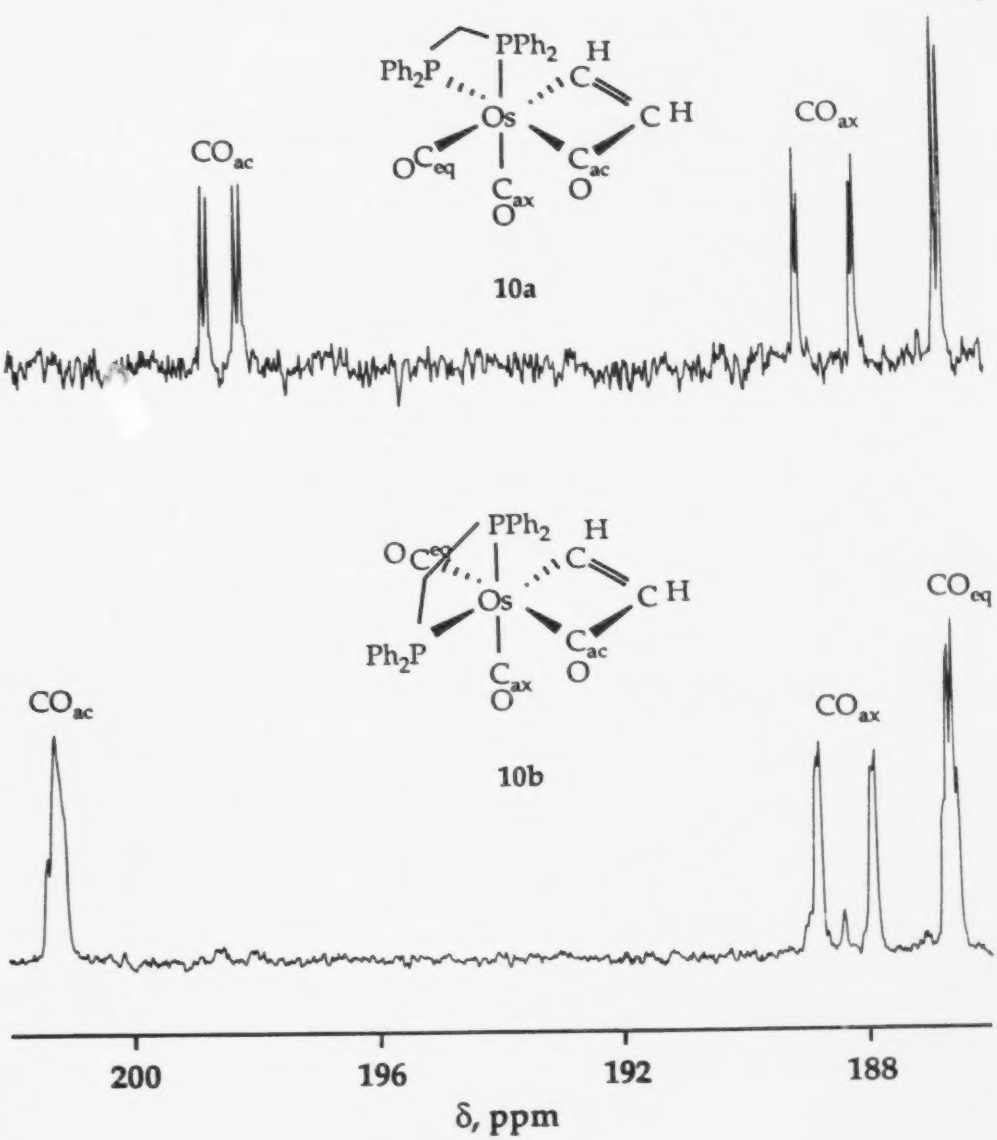


Figure 3.2: The $^{13}C\{^1H\}$ NMR Spectra of 10a (top) and 10b (bottom) in the Carbonyl Region

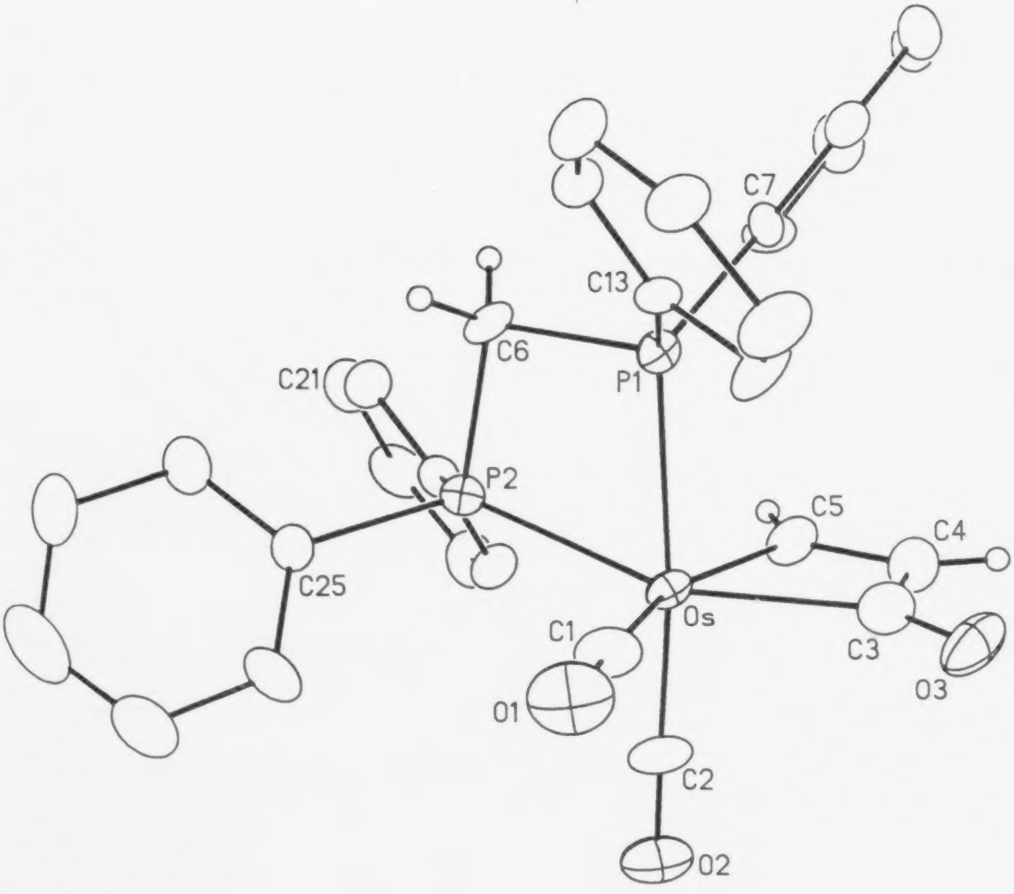

C7
C13
C6
C21
P1
P2
C5
C4
C25
Os
C1
C3
O1
O3
C2
O2

Figure 3.3: ORTEP View of $Os(CO)_2(\eta^2\text{-}COC_2H_2)(\eta^2\text{-}dppm)$, 10a

Table 3. 3: Selected Bond Distances and Angles for $Os(CO)_2(\eta^2-COC_2H_2)(\eta^2-dppm)$, 10a

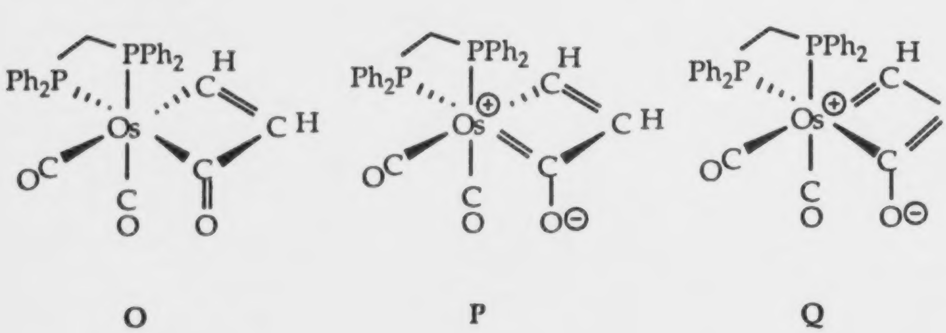
Bond Distances (Å)

Os-C(1)	1.89(1)	Os-C(2)	1.82(2)
Os-C(3)	2.13(2)	Os-C(4)	2.68(2)
Os-C(5)	2.11(1)	Os-P(1)	2.403(4)
Os-P(2)	2.381(4)	C(3)-O(3)	1.22(2)
C(3)-C(4)	1.49(2)	C(4)-C(5)	1.35(2)

Bond Angles (deg.)

P(1)-Os-P(2)	70.6(1)	P(1)-Os-C(1)	92.1(5)
P(1)-Os-C(2)	172.5(5)	P(1)-Os-C(3)	94.6(5)
P(1)-Os-C(5)	90.8(4)	C(3)-Os-C(5)	63.4(6)
P(2)-Os-C(3)	159.1(5)	Os-C(2)-O(2)	175(2)
C(1)-Os-C(5)	161.1(6)	P(1)-C(6)-P(2)	96.9(6)

bond and C-C single bond distances, respectively.[6,30,31] The C(3)O(3) bond length of 1.22 (2) Å is in the normal range of a C=O bond distance in an α,β-unsaturated ketones.[32] Thus the data are in accord with the view that the bonding in **10a** is properly represented by the osmacyclobutenone form **O**, while contributions from the resonance structures **P** and **Q** are not significant (Scheme 3.4).



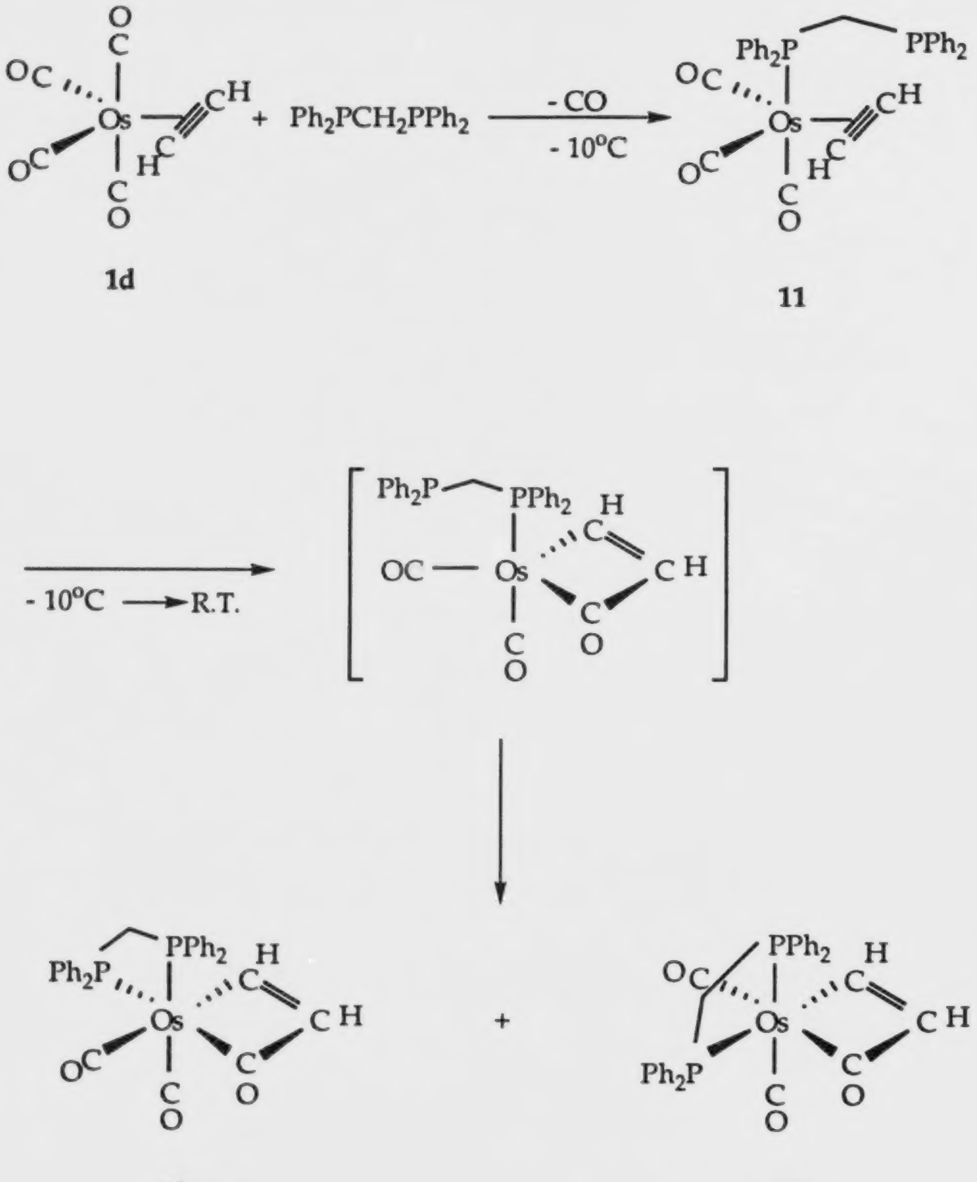
Scheme 3.4

Formation of compounds 10a and 10b. In an attempt to establish the mechanism for the formation of **10a** and **10b**, the reaction was monitored by variable temperature ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. From - 80°C to - 20°C, no intermediate was observed besides the starting materials $Os(CO)_4(\eta^2\text{-}C_2H_2)$ and dppm. At - 10°C, the $^{31}P\{^1H\}$ NMR spectrum showed a new species **11** that had two resonances at δ - 5.9 and - 28.3. The ^{31}P chemical shift of free dppm is at δ - 22.7. Thus we feel confident in assigning the resonance at δ - 28.3 to the free end of the η^1-dppm ligand and the other at δ - 5.9 to the coordinated phosphine. The chemical shifts of the uncoordinated phosphine in the closely related complexes, $Ru(CO)_4(\eta^1\text{-dppm})$[33] and $Fe(CO)_4(\eta^1\text{-dppm})$,[34] are at δ - 26.2 and - 25.7, respectively. The

^{1}H NMR spectrum of **11** showed a lowfield doublet at δ 5.63, which is characteristic of hydrogens of a coordinated acetylene. Selective ^{1}H{^{31}P} decoupling experiments clearly established that, as expected, the two protons at δ 5.63 are coupled to the phosphine at δ - 5.9. In order to obtain the carbonyl resonances, an experiment was carried out by starting with ^{13}CO enriched sample of **1d.** The ^{13}C{^{1}H} NMR spectrum of the species **11** showed two carbonyl resonances at δ 186.2 and 175.7 with an intensity ratio of 2:1, the signal at δ 175.7 also displayed a large coupling to the coordinated phosphine at δ - 5.9 with a coupling constant of 116.7 Hz, establishing their *trans* arrangement. A singlet at δ 184.2, due to free ^{13}CO, was observed also. Therefore, there is little doubt that intermediate **11** has a trigonal bypyramidal configuration as shown in the Scheme 3.5.

On warming the solution to room temperature from - 10°C, this species gradually converts to the final two isomeric products without any other additional observable intermediate. As seen in previous schemes, and also shown in the Scheme 3.5, migratory insertion of carbonyl into coordinated acetylene leads to the formation of osmacyclobutenone and leaves a vacant site for coordination of the free end of the dangling diphosphine ligand. There are two possible ways for the diphosphine to chelate, thus formation of two isomeric **10a** and **10b**.

In order to determine the effect of CO, the reaction was monitored by ^{31}P{^{1}H} and ^{1}H spectroscopy under N_2 or CO atmospheres, respectively. When the reaction was performed under a N_2 atmosphere, after 30 min at - 10°C, almost all the starting material was consumed. In the case of a CO atmosphere, only half of the starting material was converted into intermediate **11** and final products. This indicates that the rate of the reaction under a CO atmosphere is substantially slower, and implies that the reaction proceeds via CO dissociation.


1d
Ph2PCH2PPh2
- CO
- 10°C
11
- 10°C ⟶ R.T.
10a
10b

Scheme 3.5: The Mechanism for Formation of 10a/10b

3.2.4. Reactions of $Os(CO)_4(\eta^2\text{-}C_2Me_2)$ (1e) with dppm

As described above, the reaction of compound **1d** with dppm led to the formation of two isomeric products **10a** and **10b**. Surprisingly, the reaction of compound **1e** with dppm resulted in the formation of a single product **12** (eq. 3.5).

$$\mathbf{1e} \quad + \quad \text{dppm} \xrightarrow[-\,78^{\circ}C \rightarrow r.\,t.]{CH_2Cl_2} Os(CO)_2\{(CO)_2C_2Me_2)\}(dppm) \qquad (3.5)$$

12

The IR spectrum of **12** showed two terminal carbonyl bands at 2019 and 1968 cm^{-1} and an acyl band at 1581 cm^{-1}. The ^1H NMR spectrum showed two resonances at δ 1.61 and 1.19, each integrating as three protons and the methylene hydrogens showed up at δ 5.32 and 4.94, each integrating as one proton. In the $^{31}P\{^1H\}$ spectrum, two signals were observed at δ - 43.2 and - 47.6, the high field shifts compared to that of free dppm indicating the formation of a four-membered chelate ring.[24,25]

The $^{13}C\{^1H\}$ NMR spectrum (Fig. 3.4) shows two bands at δ 185.7 ($^2J_{CP}$ = 9.2 Hz) and 184.5 ($^2J_{CP}$ = 73.9 Hz, $^2J_{CP}$ = 7.2 Hz) in the typical range of terminal carbonyls.[35] More importantly, two resonances at δ 248.4 ($^2J_{CP}$ = 12.5 Hz, $^2J_{CP}$ = 5.1 Hz) and 241.0 ($^2J_{CP}$ = 56.8 Hz, $^2J_{CP}$ = 9.0 Hz) suggest the presence of two acyl groups in the molecule. The ^{13}C data, in conjunction with the large *trans* $^{31}P\text{-}^{13}C$ coupling, establishes the presence of two carbonyls and two acyl groups, one of each being *trans* to a phosphorus atom. Thus, there are two possibilities for the molecular structure (Scheme 3.6).

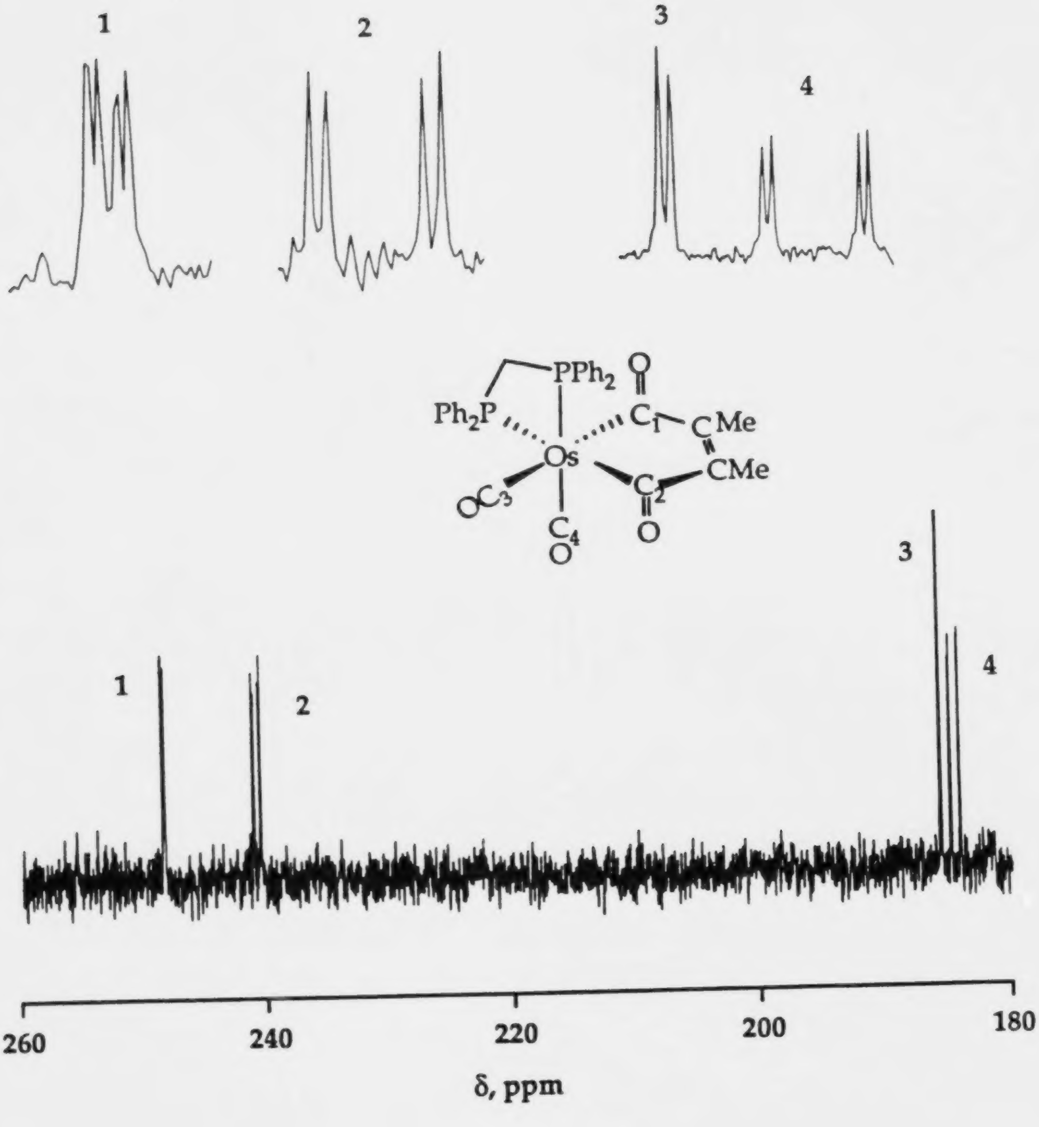
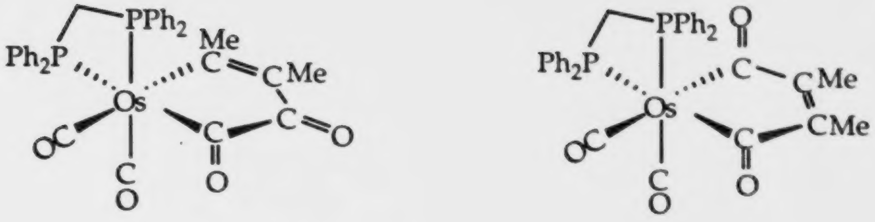


Figure 3.4: $^{13}C\{^{1}H\}$ NMR Spectra of 12 in the Carbonyl Region:

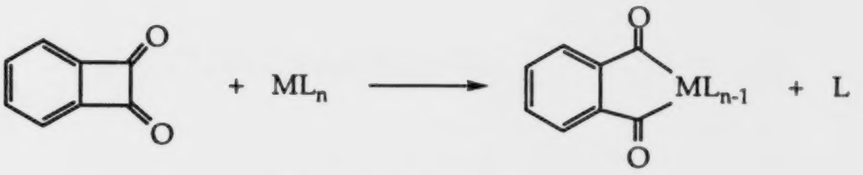
(a) Normal, (b) Expansion of the Carbonyl Resonances



R **S**

Scheme 3.6

Consecutive double insertion of carbon monoxide leading to structure **R** is very unusual, only two examples have been reported.[8,36] Complexes of structure type **S** are more common,[37-39] although not via CO insertion. Liebeskind reported the synthesis of maleoylmetal complexes from benzocyclobutenedione (eq. 3.6).[40] For both types of compounds, the chemical shifts of the acyl carbons are similar. Thus, although the molecular structure of **12** could not be unambiguously deduced from chemical shift assignments, the magnitude of the ^{31}P-^{13}C coupling favored structure **S**.



(3.6)

ML_n: $Fe(CO)_5$, $ClRh(PPh_3)_3$, $ClCo(PPh_3)_3$, $CpCo(CO)_2$

Solid State Structure of 12. To verify the molecular structure of compound **12**, an X-ray structure determination was carried out. A

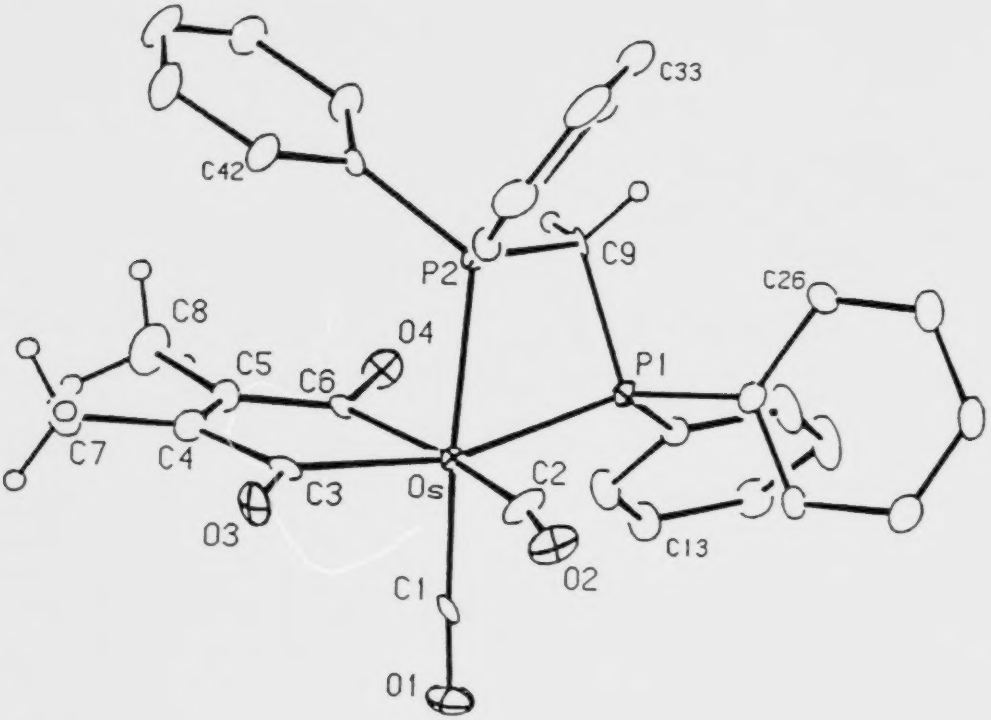

C33
C42
P2
C9
C26
C8
O4
C5
C6
P1
C7
C4
C3
Os
C2
O3
C13
O2
C1
O1

Figure 3.5: ORTEP View of $Os(CO)_2\{\eta^2-C(O)CMeCMeC(O)\}(dppm)$, 12

Table 3.4 Selected Bond Distances and Angles for $Os(CO)_2\{\eta^2\text{-}C(O)CMeCMeC(O)\}(dppm)$, 12

Bond Distances (Å)

Os-P(1)	2.403 (2)	Os-P(2)	2.389 (2)
Os-C(1)	1.884 (8)	Os-C(2)	1.931 (9)
Os-C(3)	2.081 (8)	Os-C(6)	2.135 (7)
P(1)-C(9)	1.851 (7)	P(2)-C(9)	1.844 (7)
C(1)-O(1)	1.149 (9)	C(2)-O(2)	1.15 (1)
C(3)-O(3)	1.25 (1)	C(6)-O(4)	1.316 (9)
C(3)-C(4)	1.50 (1)	C(4)-C(5)	1.36 (1)
C(5)-C(6)	1.39 (1)	C(5)-C(8)	1.49 (1)

Bond Angles (deg.)

P(1)-Os-P(2)	69.37 (6)	P(1)-Os-C(1)	99.4 (2)
P(1)-Os-C(2)	93.8 (3)	P(1)-Os-C(3)	163.9 (2)
P(1)-Os-C(6)	96.4 (2)	P(2)-Os-C(1)	164.5 (2)
P(2)-Os-C(3)	95.3 (2)	P(2)-Os-C(6)	82.2 (2)
C(1)-Os-C(2)	93.9 (3)	C(1)-Os-C(3)	94.5 (3)
C(1)-Os-C(6)	88.6 (3)	C(2)-Os-C(3)	93.3 (4)
C(2)-Os-C(6)	169.0 (3)	C(3)-Os-C(6)	75.8 (3)
Os-C(2)-O(2)	170.7 (9)	Os-C(3)-O(3)	127.8 (6)
Os-C(3)-C(4)	115.6 (6)	C(3)-C(4)-C(5)	115.0 (7)
(3)-C(4)-C(7)	119.2 (8)	C(4)-C(5)-C(6)	115.1 (7)
C(6)-C(5)-C(8)	119.2 (9)	Os-C(6)-C(4)	123.3 (5)

perspective view of compound **12** is shown in Figure 3.5. The relevant bond lengths and angles are listed in Table 3.4.

Figure 3.5 clearly shows that the molecule contains an Os-C(3)-C(4)-C(5)-C(6) osmacyclopentenedione ring. The ring is almost planar with atomic deviations from the weighted least-squares plane being less than 0.04 Å (Table 3.5). The geometry around osmium is distorted octahedral.

Table 3.5 Weighted[a] Least-squares Plane Comprising Os-C(3)-C(4)-C(5)-C(6)

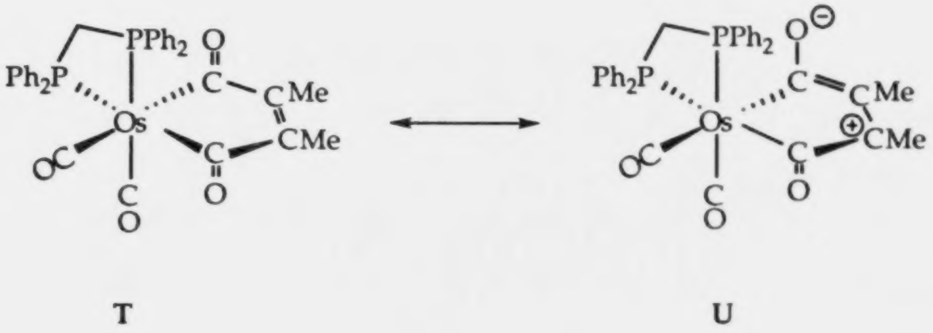
Coefficients[b]				Defining Atoms with Deviations[c]			
5.3067	8.7377	- 7.0213	1.4648	Os	0.030	C3	- 0.036
				C4	0.025	C5	0.013
				C6	- 0.031		

[a] Weights are derived from the atomic and positional esd's using the method of Hamilton (Hamilton, W. C. *Acta Crystallogr.* **1961**, 14, 185).

[b] Coefficients are for the form ax + by + cz - d = 0 where x, y, and z are crystallographic coordinates.

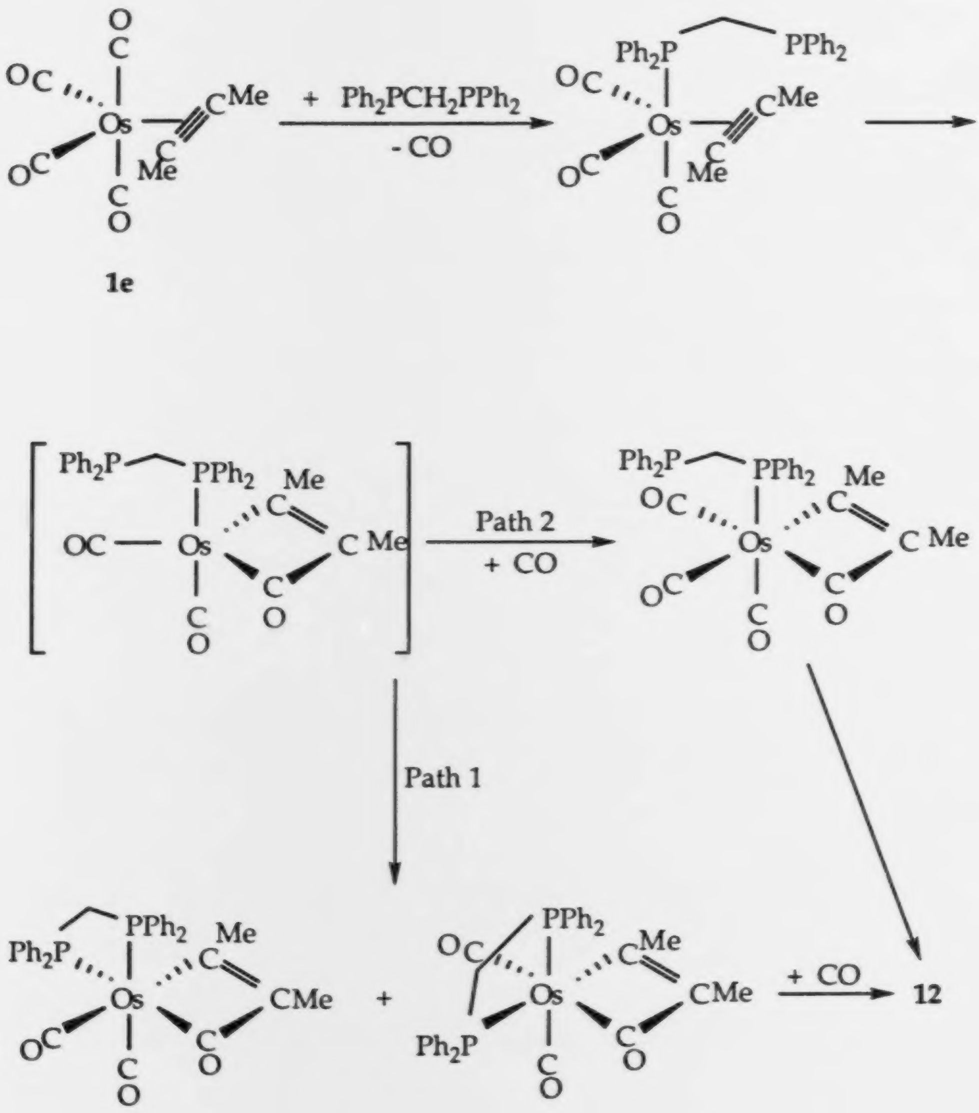
[c] Deviations are in angstroms.

The major deviations are the P(1)-Os-P(2) angle of 69.37 (6)° and C(3)-Os-C(6) angle of 75.8 (3)° (Table 3.4), which reflect the requirements of the chelating dppm ligand and the osmacycle. The Os-C(1) bond distance (1.884 (8) Å) is somewhat shorter than that of Os-C(2) (1.931 (9) Å), reflecting that the *trans* position of the former to a phosphine ligand enhanced back bonding to this carbonyl. The C(4)-C(5) bond length is 1.36 (1)Å, which is somewhat longer than that of a C-C double bond due to its conjugation with two acyl groups.[6] The Os-C(6) bond distance is 2.137 (7) Å which is almost the same as the Os-C(sp^2) bond length of 2.138 (5)Å in $Os_2(CO)_8$(μ-DMAD)[41] whereas the Os-C(3) distance (2.018 (8) Å) is much shorter than that of Os-C(6), and presumably reflects again its trans disposition to a phosphine (P(1)). Consistent with the conjugation of O(3)-C(3)-C(4)-C(5)-C(6)-O(4), the bond distances of C(3)-C(4) (1.50 (1) Å) and C(5)-C(6) (1.39 (1) Å) are between a C-C single bond (1.541 (3) Å) and a C-C double bond (1.337 (6) Å).[6] Finally, the bond distances of C(3)-O(3) (1.25 (1) Å) is in agreement with the C=O bond length of 1.23 (3) Å found in $Ru_2(CO)_4${μ-$C(O)C_2(CO_2Me)_2$}$(dmpm)_2$[8] and that of 1.24 (3) Å in OsIrCp$(CO)_5$(μ-C_2H_2CO)[42] while the C(6)-O(4) (1.316 (9) Å) bond distance is somewhat longer. These bond distances suggest that the resonance structure **U** also contributes to the bonding (Scheme 3.7).



Scheme 3.7

Formation of Compound 12. Based on the CO substitution and insertion reactions of $Os(CO)_4$(η^2-alkyne) described above, a plausible mechanism for the formation of **12** is given in Scheme 3.8. The initial step is substitution of a carbonyl by one end of the dppm ligand, followed by CO



Scheme 3.8: Proposed Mechanism for Formation of 12

insertion to generate a sixteen electron species. This intermediate is stabilized either by phosphine coordination Path 1 or through CO coordination Path 2. Since the reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with dppm proceeds through Path 1, the same pathway is more likely to be operative in this case. The next step is alkenyl migratory insertion,[43-45] followed by addition of CO to give complex **12**. Apparently the Os-C(Me) bond is sufficiently weaker to allow the facile insertion of the second CO ligand. This has been supported as the reaction of $Os(CO)_4(\eta^2\text{-}C_2Me_2)$ with dppm, even performed under strong N_2 purge, gave the product **12** rather than mono-CO inserted product.

3.3. Conclusions

The work presented in this Chapter has demonstrated that $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, alkyne = HFB; M = Os, alkyne = C_2H_2, C_2Me_2) complexes readily react with diphosphines to generate novel metallacyclic complexes. In the case of $Ru(CO)_4(\eta^2\text{-HFB})$, the reaction with dppm and dmpm results in formation of the metallabicyclic complexes $(OC)_3Ru\text{-}P(R_2)(CH)\text{-}P(R_2)\text{-}C(CF_3)\text{-}C(H)(CF_3)$ (R = Ph, **8a**; Me, **8b**) as a result of nucleophilic attack of the coordinated HFB ligand followed by remarkably facile proton abstraction. By contrast, the reaction with dppe and dmpe gives simple substitution of two CO ligands and formation of the expected $Ru(CO)_2(\eta^2\text{-}R_2PCH_2CH_2PR_2)(\eta^2\text{-HFB})$ (R = Ph, **9a**; R = Me, **9b**). This suggests that both the acidity of the methylenic hydrogens of the diphosphine ligands and the formed chelate ring size are important in facilitating nucleophilic attack by the dangling PR_2 group on the coordinated alkyne.

Consistent with the alkyne-CO coupling reactions observed between $Os(CO)_4(\eta^2-RC_2R)$ (R = H, CH_3) complexes and monophosphines, these complexes readily undergo CO insertions into metal-alkyne bonds in the presence of dppm to give the osmacyclobutenone species $Os(CO)_2\{\eta^2-C(O)CHCH\}(\eta^2$-dppm) (**10a**, **10b**) and the osmacyclopentenedione complex $Os(CO)_2\{\eta^2-C(O)C(CH_3)C(CH_3)C(O)\}(\eta^2$-dppm) (**12**). Low temperature NMR spectroscopic experiments established that the reaction of $Os(CO)_4(\eta^2-C_2H_2)$ with dppm proceeds through the CO substituted intermediate $Os(CO)_3(\eta^2-C_2H_2)(\eta^1$-dppm) (**11**), before the second phosphine coordinates to generate two isomeric species **10a** and **10b**. The pathway for formation of compound **12** is postulated to be similar to that of **10a** and **10b**. The facile insertion of the second CO in this case is attributed to the weaker Os-alkenyl bond (Os-C(Me)= vs Os-C(H)=) thereby facilitating the migratory insertion step.[46,47] Although there are several metallacyclobutenones and metallacyclopentenediones reported,[31,48-53] the osmacyclobutenones (**10a** and **10b**) and osmacyclopentenedione species **12** described in this Chapter and those presented in Chapter 2 are the first clear examples of formal CO insertion reactions into metal-based alkyne ligands.

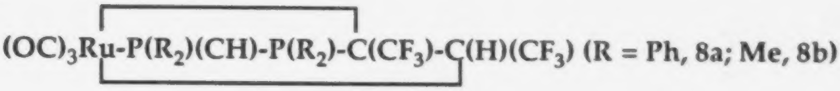
3.4. Experimental Section

3.4.1. Starting Materials and Reagents

The ligands, bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)ethane (dppe), bis(dimethylphosphino)methane (dmpm), and bis(dimethylphosphino)ethane (dmpe) were obtained from Aldrich Chemical Company; dppm and dppe were recrystallized from ethanol before use. ^{13}CO (99%) was purchased from Isotec, Inc.

3.4.2. Synthetic Procedures

Synthesis of



$(OC)_3Ru\text{-}P(R_2)(CH)\text{-}P(R_2)\text{-}C(CF_3)\text{-}C(H)(CF_3)$ **(R = Ph, 8a; Me, 8b)**

8a: To a solution of dppm (38 mg, 0.10 mmol) in CH_2Cl_2 (5 ml) was added $Ru(CO)_4(\eta^2\text{-}HFB)$ (39 mg, 0.10 mmol) at - 5 °C. The clear solution was stirred at 0°C for 1 h, followed by slow warming to room temperature over a period of 2 h. The solvent was then removed in vacuo. Recrystallization from CH_2Cl_2/pentane at - 20°C afforded 54 mg (74%) of **8a** as colorless crystals. A similar procedure was used to prepare **8b** in 70 % yield.

Data for **8a**:

IR (pentane, cm^{-1}): υ_{CO}: 2085(s), 2028(m), 2000(s).

^1H NMR: 2.85 (m, $^3J_{PH}$ = 16 Hz, $^3J_{FH}$ = 9 Hz, 1H), 0.69 (dd, $^2J_{PH}$ = 9 Hz, $^2J_{PH}$= 18 Hz, 1H).

$^{31}P\{^1H\}$ NMR: 32.9 (d, $^2J_{PP}$ = 84 Hz), 47.7 (dq, $^2J_{PP}$ = 84 Hz, $^3J_{PF}$ = 6 Hz).

^{19}F NMR : - 43.3 (dq, $^5J_{FF}$ = 10 Hz, $^3J_{PF}$ = 6 Hz), - 48.8 (dq, $^5J_{FF}$ = 10 Hz, $^3J_{FH}$ = 9 Hz).

$^{13}C\{^1H\}$ NMR: 198.7 (d, $^2J_{PC}$ = 14 Hz, $C_{eq}O$), 195.9 (d, $^2J_{PC}$ = 7.5 Hz, $C_{eq}O$), 192.2 (d, $^2J_{PC}$ = 83 Hz, $C_{ax}O$).

Anal. Calcd for $C_{32}H_{22}F_6O_3P_2Ru$: C, 52.54; H, 3.03. Found: C, 52.41; H, 2.87.

Mass Spectrum (70 ev, 220°C, m/e): M^+ - nCO, n = 0-3.

Data for **8b**:

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2080(s), 2018(m), 1988(s).

^1H NMR (- 70°C): 3.8 (br, 1H), 2.8 (br, 1H), 1.6 (br, 12H).

$^{31}P\{^1H\}$ NMR (- 70°C): 7.0 (d, $^2J_{PP}$ = 75 Hz), 40.1 (dq, $^2J_{PP}$ = 75 Hz, $^3J_{PF}$ = 8 Hz).

^{19}F NMR (- 70°C): - 46.5 (dq, $^5J_{FF}$ = 9 Hz, $^3J_{PF}$ = 8 Hz), - 49.9 (dq, $^5J_{FF}$ = 9 Hz, $^3J_{HF}$ = 10 Hz).

$^{13}C\{^1H\}$ NMR (- 70°C): 197.9 (d, $^2J_{PC}$ = 13 Hz, $C_{eq}O$), 196.5 (s, $C_{eq}O$), 192.3 (d, $^2J_{PC}$ = 81 Hz, $C_{ax}O$).

Anal. Calcd for $C_{12}H_{14}O_3P_2F_6Ru.0.5\ CH_2Cl_2$: C, 28.56; H, 2.88. Found: C, 28.77; H, 2.48.

Synthesis of $Ru(CO)_2(\eta^2\text{-}R_2PCH_2CH_2PR_2)(\eta^2\text{-HFB})$ (R = Ph, 9a; R = Me, 9b)

9a: A solution of dppe (78.6 mg, 0.197 mmol) in 10 ml CH_2Cl_2 was added to a solution of $Ru(CO)_4(\eta^2\text{-HFB})$ (74 mg, 0.197 mmol) in 10 ml CH_2Cl_2 at 0°C. The stirred solution was allowed to slowly warm to room temperature over a period of 3 h and was stirred at room temperature for 30 min. The solvent was then removed at - 40°C. The residue was dissolved in CH_2Cl_2 and purified by silica gel chromatography. Elution with a mixture of CH_2Cl_2/hexane (2/3) afforded 87 mg (64%) of the product

9a. Complex **9b** was prepared similarly in 60% yield except recrystallization from CH_2Cl_2/pentane.

Data for **9a**:

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2027(s), 1961(s); $\upsilon_{C\equiv C}$: 1772(w).

^1H NMR: 2.47 (m, 1H), 2.84 (m, 1H), 2.92 (m, 1H), 3.03 (m, 1H).

$^{31}P\{^1H\}$ NMR: 65.3 (dq, $^3J_{PP}$ = 16.5 Hz, $^4J_{PF}$ = 9.2 Hz), 54.4 (d, $^3J_{PP}$ = 16.5 Hz).

^{19}F NMR: - 53.4 (q, $^5J_{FF}$ = 6.0 Hz), - 54.7 (dq, $^5J_{FF}$ = 6.0 Hz, $^4J_{PF}$ = 9.2 Hz).

$^{13}C\{^1H\}$ NMR: 203.8 (d, $^2J_{CP}$ = 13.1 Hz, $C_{eq}O$), 195.6 (dd, $^2J_{CP}$ = 118.2 Hz, $^2J_{CP}$ = 5.0 Hz, $C_{ax}O$).

Anal. Calcd for $C_{32}H_{24}O_2P_2F_6Ru$: C, 53.56; H, 3.37. Found: C, 53.36, H, 3.08.

Mass Spectrum (70 ev, 220°C, m/e): M^+ - nCO, n = 0-2.

Data for **9b**:

IR (pentane, cm^{-1}): υ_{CO}: 2028(s), 1959(s); $\upsilon_{C\equiv C}$: 1785(w).

^1H NMR (- 70°C): 1.74 (d, $^2J_{PH}$ = 10 Hz, 3 H), 1.64 (d, $^2J_{PH}$ = 8 Hz, 3 H), 1.38 (d, $^2J_{PH}$ = 9 Hz, 3 H), 0.88 (d, $^2J_{PH}$ = 10 Hz, 3 H), 1.90 (m, 2 H), 1.59 (m, 2 H).

$^{31}P\{^1H\}$ NMR (- 70°C): 41.2 (m, $^3J_{PP}$ = 20 Hz, $^4J_{PF}$ = 6 Hz), 35.3 (d, $^3J_{PP}$ = 20 Hz).

^{19}F NMR (- 70°C): - 55.2 (dq, $^5J_{FF}$ = 6 Hz, $^3J_{PF}$ = 6 Hz), - 53.5 (q, $^5J_{FF}$ = 6 Hz).

$^{13}C\{^1H\}$ NMR (- 70°C): 204.4 (dm, $^2J_{CP}$ = 14 Hz, $C_{eq}O$), 195.5 (dm, $^2J_{CP}$ = 120 Hz, $C_{ax}O$).

Anal. Calcd for $C_{12}H_{16}O_2P_2F_6Ru$: C, 30.71; H, 3.18. Found: C, 31.00; H, 3.18.

Mass Spectrum (70 ev, 220°C, m/e): M^+ - nCO, n = 0-2.

Synthesis of $Os(CO)_2\{\eta^2\text{-}C(O)CHCH\}(\eta^2\text{-dppm})$, 10a; 10b

A solution of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ (75.6 mg, 0.230 mmol) in dichloromethane (10 ml) at - 78°C was added to a solution of dppm (88.6 mg, 0.230 mmol) in dichloromethane (10 ml) at - 78°C. The reaction mixture was stirred vigorously and allowed to slowly warm to room temperature for a period of 3 h. After the solvent was removed in vacuo at - 20°C, the residue was separated by silica gel column chromatography using a THF/hexane (7/3) mixture to give 69.4 mg yellow solids of **10a** (44%) and 52.6 mg (32%) orange solids of **10b**.

Data for **10a**:

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2009 (vs), 1948 (s); υ_{acyl}: 1633 (w).

^1H NMR: 5.4 (m, $^2J_{HH}$ = 15.7 Hz, $^2J_{HP}$ = 8.6 Hz, $^2J_{HP}$ = 8.0 Hz, 1H, $Ph_2PCH_2PPh_2$), 4.8 (m, $^2J_{HH}$ = 15.7 Hz, $^2J_{HP}$ = 9.4 Hz, $^2J_{HP}$ = 8.8 Hz, 1H, $Ph_2CH_2PPh_2$).

$^{31}P\{^1H\}$ NMR: - 45.6 (d, $^2J_{PP}$ = 4 Hz), - 50.6 (d, $^2J_{PP}$ = 4 Hz);

$^{13}C\{^1H\}$ NMR: 198.5 (dd, $^2J_{CP}$ = 54 Hz, $^2J_{CP}$ = 9 Hz, COacyl), 188.5 (dd, $^2J_{CP}$ = 94 Hz, $^2J_{CP}$ = 5 Hz, COax), 186.7 (d, $^2J_{CP}$ = 8 Hz, COeq), 165.9 (dd, $^3J_{CP}$ = 30.9 Hz, $^3J_{CP}$ = 8.3 Hz, Os-C(O)CH), 153.3 (dd, $^2J_{CP}$ = 11.7 Hz, $^2J_{CP}$ = 6.0 Hz, OsCH).

Anal. Calcd for $C_{30}H_{24}O_3P_2Os\cdot0.5CH_2Cl_2$: C, 50.38; H, 3.47, Cl, 4.88. Found: C, 50.59, H, 3.43, Cl, 4.44. One half equivalent of CH_2Cl_2 was also verified from crystal structure determination.

Mass Spectrum (70ev, 200°C, m/e): M^+ - nCO, n = 0 - 2.

Data for **10b**:

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2002 (vs), 1946 (s); υ_{acyl}: 1630 (w).

^1H NMR (δ, CD_2Cl_2): 9.2 (ddd, $^3J_{HH}$ = 6.0 Hz, $^3J_{HP}$ = 3.7 Hz, $^3J_{HP}$ = 1.4 Hz, 1H, OsCH), 8.05 (m, $^3J_{HH}$ = 6.0 Hz, $^4J_{HP}$ = 2.1 Hz, $^4J_{HP}$ = 5.9 Hz, 1H, OsCHCH), 5.2 (m, $^2J_{HH}$ = 14.7 Hz, $^2J_{HP}$ = 5.1 Hz, $^2J_{HP}$ = 4.8 Hz, 1H,

$Ph_2PCH_2PPh_2$), 4.8 (m, $^2J_{HH}$ = 14.7 Hz, $^2J_{HP}$ = 6.2Hz, $^2J_{HP}$ = 6.2 Hz, 1H, $Ph_2PCH_2PPh_2$).

$^{31}P\{^1H\}$ NMR: - 41.9 (d, $^2J_{PP}$ = 13 Hz), - 39.9 (d, $^2J_{PP}$ = 13 Hz).

$^{13}C\{^1H\}$ NMR: 201.4 (m, $^2J_{CO\text{-}CO(trans)}$ = 17 Hz, $^2J_{CO\text{-}CO(cis)}$ = 4 Hz, COacyl), 188.3 (dd, $^2J_{CP}$ = 92 Hz, $^2J_{CP}$ = 6 Hz, COax), 186.7 (m, $^2J_{CO\text{-}CO(trans)}$= 17 Hz, $^2J_{CO\text{-}CO(cis)}$ = 2 Hz, COeq).

Anal. Calcd for $C_{30}H_{24}O_3P_2Os{\cdot}0.5CH_2Cl_2$: C, 50.38; H, 3.47. Found: C, 50.28; H, 3.47. The amount of CH_2Cl_2 was established from ^1H NMR spectrum in d_8-toluene.

Mass Spectrum (70 ev, 200°C, m/e): M^+ - nCO, n = 0 - 2.

Characterization of $Os(CO)_3(\eta^2\text{-}C_2H_2)(\eta^1\text{-dppm})$, 11

^1H NMR: 5.63 (d, $^3J_{HP}$ = 3.0 Hz, C_2H_2), 2.85 (dd, $^2J_{HP}$ = 10.6 Hz, $^2J_{HP}$ = 2.2 Hz, $PPh_2CH_2PPh_2$).

$^{31}P\{^1H\}$ NMR: - 28.3 (d, $^2J_{PP}$ = 101.6 Hz), - 5.9 (d, $^2J_{PP}$ = 101.6 Hz).

$^{13}C\{^1H]$ NMR: 186.2 (d, $^2J_{CP}$ = 11.1 Hz, 2 CO), 175.7 (d, $^2J_{CP}$ = 116.7 Hz, CO).

Synthesis of $Os(CO)_2\{\eta^2\text{-}C(O)C(CH_3)C(CH_3)C(O)\}(\eta^2\text{-dppm})$, 12

A colorless solution of dppm (45 mg, 0.118 mmol) in 10 ml CH_2Cl_2 was added to a solution of $Os(CO)_4(\eta^2\text{-}C_2Me_2)$ (42 mg, 0.118 mmol) at - 78°C. The solution was allowed to slowly warm to room temperature over a period of 4 h. The clear solution gradually changed to white suspension, then to a yellow solution. After being stirred for additional 1 h, the solvents were removed in vacuo. Recrystallization from CH_2Cl_2/pentane yielded 83 mg (85%) of a pale yellow powder of **12**.

IR (CH_2Cl_2/pentane, cm-1): υ_{CO}: 2019 (vs), 1968 (s); υ_{acyl}: 1581 (m).

^{1}H NMR: 5.32 (m, $^2J_{HH}$ = 14.9 Hz, $^2J_{PH}$ = 7.6 Hz, $^2J_{PH}$ = 6.4 Hz, $Ph_2PCH_2PPh_2$), 4.94 (m, $^2J_{HH}$ = 14.9 Hz, $^2J_{PH}$ = 10.0 Hz, $^2J_{PH}$ = 9.6 Hz, $PPh_2CH_2PPh_2$), 1.61 (s, $OsC(O)C(CH_3)=$), 1.19 (s, $OsC(O)C(CH_3)=$).

$^{31}P\{^1H\}$ NMR: - 43.2 (d, $^2J_{PP}$ = 17.4 Hz), - 47.6 (d, $^2J_{PP}$ = 17.4 Hz).

$^{13}C\{^1H\}$ NMR: 248.4 (dd, $^2J_{CP}$ = 12.5 Hz, 2J_{CP} = 5.1 Hz, $C_{acyl}O$), 240.8 (dd, $^2J_{CP}$ = 56.8 Hz, $^2J_{CP}$ = 9.0 Hz, $C_{acyl}O$), 185.7 (d, $^2J_{CP}$ = 9.2 Hz, $C_{ae}O$), 184.5 (dd, $^2J_{CP}$ = 73.9 Hz, $^2J_{CP}$ = 7.2 Hz, $C_{ac}O$), 167.3 (d, $^3J_{CP}$ = 20.7 Hz, $OsC(O)C(CH_3)=$), 166.8 (s, $OsC(O)C(CH_3)=C(CH_3)-$), 42.2 (dd, $^1J_{CP}$ = 30.7 Hz, $^1J_{CP}$ = 24.9 Hz, $PPh_2CH_2PPh_2$), 10.1 (s, $OsC(O)C(CH_3)=$), 9.7 (s, $OsC(O)C(CH_3)=C(CH_3)-$).

Anal. Calcd for $C_{33}H_{28}O_4P_2Os$: C, 53.51; H, 3.81. Found: C, 52.95; H, 3.55.

Variable Temperature NMR Monitoring the Reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with dppm. In a typical experiment, a solution of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ (21.4 mg, 0.065 mmol) in CD_2Cl_2 (0.7 ml) was added via a cannula into an NMR tube containing dppm (25 mg, 0.065 mmol) under argon at - 78 °C. The NMR tube was then transfered into the NMR probe at - 80°C. The reaction was monitored by ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The various NMR spectra were recorded from - 80°C to ambient temperature with an increment of 10°C.

3.4.3. X-ray Structure Determination of 8a

A colorless single crystal was grown by cooling a CH_2Cl_2/pentane solution of **8a** at - 20°C. The X-ray data collection and structure refinement were carried out by Dr. Andrew Bond and Prof. Robin Rogers at Northern Illinois University. The crystal was mounted in a thin-walled glass capillary under argon and transfered to the goniometer. The structure was solved in the space group $P2_1/c$ by using standard Patterson and Fourier techniques. All non-hydrogen atoms were located. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom. The hydrogens H (1) C(4) and H(2) C(6) were located from a difference Fourier map and included with fixed contributions (B = 5.5 Å^2). A summary of data collection parameters is given in Table 3.4. The final atomic coordinates are given in Table 3.6. The selected bond distances and angles are given in Table 3.1.

3.4.4. X-ray Structure Determination of 10a

Yellow crystals of compound **10a** suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from a solution of **10a** in a CH_2Cl_2/pentane mixture at - 20 °C. The X-ray data collection and structure refinement were carried out by Dr. Andrew Bond and Prof. Robin Rogers at Northern Illinois University. A single crystal of **10a** was mounted in a thin-walled glass capillary flushed with Ar and transferred to the goniometer. A summary of data collection parameters is given in Table 3.8. Least-square refinement with isotropic thermal parameters led to R = 0.088. The solvent molecule was found to be disordered about a crystallographic center of inversion. The disorder placed Cl (1) and C (31) in essentially the same position and it was not possible to resolve them. This position was refined as a 1/2 weighted Cl and 1/2 weight C. Cl (2) was also refined at half occupancy. All non-hydrogen atoms were located. The hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The final values of the positional parameters are given in Table 3.9.

Table 3.6: Crystal Data and Summary of Data Collection and Structure Refinement for 8a

formula	$C_{32}H_{22}F_6O_3P_2Ru$
formula wt.	731.54
crystal size, mm	0.10 x 0.15 x 0.35
space group	$P2_1/C$
temperature, °C	20
unit cell parameters	
a, Å	10.776 (3)
b, Å	18.248 (6)
c, Å	15.756 (9)
β, deg.	93.86 (5)
V, Å^3	3091
Z	4
D_{calc}, g cm^{-3}	1.57
μ_{calc}, cm^{-1}	6.74
diffractometer	Enraf-Nonius CAD-4
radiation	MoK_α (λ= 0.71073)
monochrometer	graphite
scan type	ω-2ø
scan width	0.80 + 0.35tanø
take-off angle, deg.	2.0
maximum 2 ø, deg.	50.0
reflections measured	5913
reflections observed	2386
No. of parameters varied	397

R[a]	0.067
R_w[b]	0.085
GOF[c]	1.82

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $Rw = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2)^{1/2}$

[c] $GOF = \{\Sigma\omega(|F_o| - |F_c|)^2/(NO - NV)\}^{1/2}$

Table 3.7: Final Fractional Coordinates for 8a

atom	x/a	y/b	z/c	B(eqv), Å
Ru	0.12322 (9)	0.46345 (6)	0.75340 (7)	2.27
P(1)	0.2663 (3)	0.4912 (2)	0.8714 (2)	2.15
P(2)	0.4236 (3)	0.4952 (2)	0.7266 (2)	2.19
F(1)	0.0139 (7)	0.5739 (5)	0.5925 (6)	4.64
F(2)	0.0774 (8)	0.6622 (5)	0.6718 (6)	4.52
F(3)	0.1811 (8)	0.6305 (5)	0.5670 (6)	4.60
F(4)	0.1631 (7)	0.4726 (5)	0.5371 (5)	3.97
F(5)	0.3610 (8)	0.4758 (5)	0.5394 (5)	4.05
F(6)	0.2718 (8)	0.3841 (4)	0.5886 (5)	3.85
O(1)	-0.089 (1)	0.5208 (7)	0.8510 (8)	5.37
O(2)	0.129 (1)	0.2992 (6)	0.790 (1)	6.87
O(3)	-0.071 (1)	0.4180 (8)	0.6105 (8)	5.70
C(1)	-0.008 (2)	0.4972 (9)	0.817 (1)	3.53
C(2)	0.131 (1)	0.3608 (9)	0.781 (1)	3.83
C(3)	0.005 (1)	0.439 (1)	0.659 (1)	4.15
C(4)	0.405 (1)	0.5119 (7)	0.8285 (9)	2.38
C(5)	0.115 (2)	0.6204 (9)	0.631 (1)	3.55
C(6)	0.194 (1)	0.5586 (8)	0.6937 (8)	2.67
C(7)	0.269 (1)	0.4919 (7)	0.6685 (8)	2.35
C(8)	0.263 (1)	0.4569 (8)	0.5854 (8)	2.91
C(9)	0.288 (1)	0.4167 (7)	0.9478 (8)	2.36
C(10)	0.405 (1)	0.3913 (8)	0.9738 (9)	3.09
C(11)	0.423 (1)	0.3363 (8)	1.033 (1)	3.56

C(12)	0.324 (2)	0.3055 (9)	1.068 (1)	4.31
C(13)	0.206 (2)	0.3312 (9)	1.044 (1)	4.12
C(14)	0.189 (1)	0.3835 (8)	0.985 (1)	3.27
C(15)	0.226 (1)	0.5665 (7)	0.9407 (8)	2.54
C(16)	0.265 (1)	0.5646 (8)	1.026 (1)	3.58
C(17)	0.241 (2)	0.624 (1)	1.077 (1)	4.74
C(18)	0.184 (2)	0.686 (1)	1.047 (2)	5.45
C(19)	0.143 (2)	0.6862 (9)	0.962 (1)	4.84
C(20)	0.169 (1)	0.6274 (7)	0.908 (1)	3.64
C(21)	0.523 (1)	0.5651 (8)	0.6835 (9)	2.76
C(22)	0.642 (1)	0.5724 (8)	0.724 (1)	3.52
C(23)	0.720 (1)	0.625 (1)	0.695 (1)	4.46
C(24)	0.687 (2)	0.6672 (9)	0.624 (1)	4.25
C(25)	0.571 (2)	0.6600 (8)	0.586 (1)	3.89
C(26)	0.489 (1)	0.6082 (7)	0.6152 (9)	2.90
C(27)	0.503 (1)	0.4091 (7)	0.7062 (8)	2.22
C(28)	0.477 (1)	0.3481 (7)	0.7555 (8)	2.70
C(29)	0.536 (1)	0.2821 (7)	0.744 (1)	3.49
C(30)	0.620 (1)	0.2769 (8)	0.682 (1)	3.45
C(31)	0.648 (1)	0.3347 (8)	0.633 (1)	3.95
C(32)	0.586 (1)	0.4023 (8)	0.645 (1)	3.43

Table 3.8: Crystal Data and Summary of Data Collection and Structure Refinement for 10a

formula	$C_{30}H_{24}O_3OsP_2 \cdot 0.5(CH_2Cl_2)$
formula wt.	727.14
crystal size, mm	0.08 x 0.15 x 0.20
space group	$P\bar{1}$
temperature, °C	19
unit cell parameters	
a, Å	9.502 (4)
b, Å	9.889 (2)
c, Å	15.706 (6)
α, deg.	81.26 (2)
β, deg.	83.94 (3)
γ, deg.	83.43 (3)
V, $Å^3$	1443
Z	2
D_{calc}, g cm^{-3}	1.67
μ_{calc}, cm^{-1}	49.1
diffractometer	Enraf-Nonius CAD-4
radiation	MoK_α (λ= 0.71073)
monochrometer	graphite
scan type	ω-2ø
scan width	0.80 + 0.35tanø
take-off angle, deg.	2.0
maximum 2 ø, deg.	50.0
reflections measured	5067

reflections observed	2766
No. of parameters varied	333
R^a	0.049
$R_w{}^b$	0.053
GOF^c	0.70

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

$^bRw = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o{}^2)^{1/2}$

$^cGOF = [\Sigma\omega(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$

Table 3.9: Final Fractional Coordinates for 10a

atom	x/a	y/b	z/c	B(eqv)a
Os	0.09880 (7)	0.60271 (6)	0.75719 (4)	2.45
P(1)	0.0446 (4)	0.7478 (4)	0.6252 (2)	2.39
P(2)	0.1069 (3)	0.8368 (4)	0.7742 (2)	2.45
O(1)	0.407 (1)	0.540 (1)	0.6919 (9)	6.46
O(2)	0.145 (1)	0.456 (1)	0.9368 (9)	5.98
O(3)	0.070 (1)	0.327 (1)	0.6875 (8)	5.30
C(1)	0.292 (2)	0.566 (2)	0.715 (1)	3.82
C(2)	0.133 (2)	0.513 (2)	0.864 (1)	4.30
C(3)	0.022 (2)	0.426 (2)	0.723 (1)	4.46
C(4)	-0.126 (2)	0.460 (2)	0.761 (1)	5.05
C(5)	-0.119 (2)	0.580 (2)	0.791 (1)	3.50
C(6)	0.068 (1)	0.910 (1)	0.6610 (8)	2.77
C(7)	-0.133 (1)	0.773 (1)	0.5860 (9)	2.44
C(8)	-0.158 (1)	0.758 (1)	0.5030 (9)	2.83
C(9)	-0.290 (2)	0.781 (2)	0.476 (1)	4.29
C(10)	-0.404 (1)	0.816 (2)	0.533 (1)	3.65
C(11)	-0.385 (2)	0.831 (2)	0.617 (1)	4.41
C(12)	-0.251 (1)	0.805 (1)	0.646 (1)	3.24
C(13)	0.164 (1)	0.733 (1)	0.5283 (8)	2.18
C(14)	0.213 (2)	0.598 (1)	0.512 (1)	3.99
C(15)	0.300 (2)	0.579 (2)	0.439 (1)	4.24
C(16)	0.337 (2)	0.694 (2)	0.3816 (9)	3.13
C(17)	0.287 (1)	0.825 (1)	0.396 (1)	3.28

C(18)	0.198 (1)	0.840 (1)	0.4696 (9)	2.90
C(19)	-0.024 (1)	0.920 (1)	0.8467 (9)	2.62
C(20)	-0.069 (1)	1.058 (1)	0.834 (1)	3.23
C(21)	-0.161 (2)	1.118 (2)	0.896 (1)	4.40
C(22)	-0.209 (2)	1.040 (2)	0.969 (1)	4.58
C(23)	-0.169 (2)	0.900 (2)	0.983 (1)	3.96
C(24)	-0.078 (2)	0.839 (2)	0.9233 (9)	3.43
C(25)	0.269 (1)	0.910 (1)	0.7923 (9)	2.74
C(26)	0.284 (2)	1.044 (2)	0.770 (1)	4.00
C(27)	0.409 (2)	1.098 (2)	0.787 (1)	5.47
C(28)	0.513 (2)	1.007 (3)	0.827 (1)	6.23
C(29)	0.500 (2)	0.870 (3)	0.846 (1)	5.48
C(30)	0.377 (2)	0.824 (2)	0.828 (1)	4.33
C(31)/Cl(1)	0.454 (2)	0.536 (2)	1.042 (1)	18.2 (6) [b]
Cl (2)	0.500 (2)	0.615 (2)	1.087 (2)	17.5 (7) [b]

[a] B(eqv) = $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

[b] Isotropic refinement.

3.4.5. X-ray Structure Determination of 12

Orange crystals of compound **12** suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from a solution of **12** in a CH_2Cl_2/pentane mixture at - 20 °C. The X-ray data collection and structure refinement was carried out by Dr. R. McDonald at the Structure Determination Laboratory, Department of Chemistry, University of Alberta. A single crystal of **12** was mounted on a glass fiber with epoxy, and optically centered in the X-ray beam of the diffractometer. The crystal was cooled to - 50°C using a cold air stream apparatus and all measurements were made at this temperature. The positions of most of the non-hydrogen atoms of the complex were found using the direct methods program SHELXS-86. The remaining non-hydrogen atoms were located from a series of difference Fourier maps. The hydrogen atoms were generated at idealized calculated positions by assuming a C-H bond length of 0.95 Å and the appropriate sp^2 or sp^3 geometry. A summary of crystallographic experimental details, data collection, and refinement conditions is given in Table 3.10. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3.11.

Table 3.10: Crystal Data and Summary of Data Collection and Structure Refinement for 12

formula	$C_{34}H_{30}Cl_2O_4OsP_2$
formula wt.	825.67
crystal size, mm	0.24 x 0.23 x 0.14
space group	$P\bar{1}$
temperature, °C	- 50°C
unit cell parameters	
a, Å	8.856 (2)
b, Å	11.056 (2)
c, Å	18.035 (3)
α, deg.	83.69 (1)
β, deg.	83.58 (1)
γ, deg.	69.40 (1)
V, $Å^3$	1637.8 (6)
Z	2
D_{calc}, g cm^{-3}	1.674
μ_{calc}, cm^{-1}	41.94
diffractometer	Enraf-Nonius CAD-4
radiation	MoK_{α} (λ= 0.71073)
monochrometer	graphite
scan type	ø-2ø
scan width	0.50 + 0.344tanø
take-off angle, deg.	3.0
maximum 2 ø, deg.	50.0
reflections measured	5709

reflections observed	4645
No. of parameters varied	388
R[a]	0.045
R_w[b]	0.069
GOF[c]	2.098

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

[b] $Rw = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2)^{1/2}$

[c] $GOF = \{\Sigma\omega(|F_o| - |F_c|)^2/(NO - NV)\}^{1/2}$

Table 3.11: Final Fractional Coordinates for 12

atom	x/a	y/b	z/c	B(eqv), Å
Os	0.32262 (5)	0.21817 (4)	0.30250 (2)	1.463 (8)
C191	0.0785 (7)	0.3325 (6)	0.8720 (4)	10.7 (2)
C192	0.0426 (8)	0.0827 (7)	0.9010 (5)	13.3 (3)
P1	0.5885 (3)	0.1653 (2)	0.3440 (1)	1.66 (6)
P2	0.4713 (3)	0.3335 (2)	0.2245 (1)	1.71 (6)
O1	0.224 (1)	0.0100 (8)	0.3975 (5)	4.5 (3)
O2	0.143 (1)	0.4225 (8)	0.4143 (5)	4.1 (3)
O3	-0.0119 (9)	0.3657 (8)	0.2533 (5)	3.5 (2)
O4	0.541 (1)	0.0102 (8)	0.2010 (4)	3.3 (2)
C1	0.258 (1)	0.090 (1)	0.3605 (6)	1.9 (2)
C2	0.222 (2)	0.347 (1)	0.3736 (6)	3.5 (3)
C3	0.123 (1)	0.281 (1)	0.2390 (6)	2.5 (3)
C4	0.145 (1)	0.217 (1)	0.1673 (6)	3.0 (3)
C5	0.289 (1)	0.119 (1)	0.1562 (6)	2.9 (3)
C6	0.394 (1)	0.0952 (9)	0.2121 (6)	2.0 (2)
C7	0.016 (1)	0.267 (1)	0.1139 (7)	4.3 (4)
C8	0.343 (2)	0.043 (1)	0.0887 (7)	5.2 (4)
C9	0.670 (1)	0.2265 (9)	0.2545 (5)	1.8 (2)
C11	0.726 (1)	0.003 (1)	0.3681 (6)	2.0 (3)
C12	0.689 (1)	-0.103 (1)	0.3526 (7)	3.1 (3)
C13	0.792 (1)	-0.229 (1)	0.3733 (7)	3.2 (3)
C14	0.927 (1)	-0.247 (1)	0.4109 (7)	3.3 (3)
C15	0.961 (2)	-0.141 (1)	0.4271 (8)	4.4 (4)

C16	0.863 (1)	-0.017 (1)	0.4069 (8)	3.7 (3)
C21	0.614 (1)	0.2568 (9)	0.4152 (6)	1.9 (2)
C22	0.537 (1)	0.248 (1)	0.4855 (6)	2.2 (3)
C23	0.560 (1)	0.309 (1)	0.5449 (6)	2.9 (3)
C24	0.659 (1)	0.379 (1)	0.5344 (6)	2.7 (3)
C25	0.738 (1)	0.391 (1)	0.4643 (6)	2.9 (3)
C26	0.721 (1)	0.331 (1)	0.4059 (6)	2.3 (3)
C31	0.444 (1)	0.4991 (9)	0.2411 (5)	2.2 (3)
C32	0.568 (1)	0.548 (1)	0.2355 (6)	2.8 (3)
C33	0.538 (2)	0.679 (1)	0.2426 (7)	3.9 (4)
C34	0.373 (2)	0.761 (1)	0.2539 (7)	4.8 (4)
C35	0.250 (2)	0.712 (1)	0.2601 (7)	3.9 (4)
C36	0.285 (1)	0.584 (1)	0.2542 (6)	2.6 (3)
C41	0.476 (1)	0.3384 (9)	0.1235 (6)	2.0 (2)
C42	0.342 (2)	0.421 (1)	0.0879 (6)	3.4 (3)
C43	0.335 (2)	0.423 (1)	0.0110 (7)	4.6 (4)
C44	0.466 (2)	0.346 (2)	-0.0312 (7)	5.0 (4)
C45	0.593 (2)	0.266 (1)	0.0020 (7)	4.2 (4)
C46	0.603 (2)	0.260 (1)	0.0802 (6)	3.3 (3)
C91	0.164 (3)	0.178 (3)	0.880 (2)	15.1 (3)

3.5. References

(1) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(2) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.

(3) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1987**, 662.

(4) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 741.

(5) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1185.

(6) *International Tables for X-ray Crystallography*; The Kynoch Press: Birminghan, England, 1962; Vol. III, pp 275-276.

(7) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

(8) Johnson, K. A.; Gladfelter, W. *Organometallics* **1992**, *11*, 2534.

(9) Field, J. S.; Haines, R. J.; Sundermeyer, J.; Woollam, S. F. *J. Chem. Soc., Dalton Trans.* **1993**, 3749.

(10) Awang, M. R.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2091.

(11) Balch, A. L.; Oram, D. E. *Organometallics* **1986**, *5*, 2159.

(12) Brauer, D. J.; Hietkamp, S.; Stelzer, O. *J. Organomet. Chem.* **1986**, *299*, 137.

(13) Brown, M. P.; Yavari, A.; Manojlovic-Muir, L.; Muir, K. W.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1982**, *236*, C33.

(14) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *J. Organomet. Chem.* **1973**, *60*, C39.

(15) Issleib, V. K.; Abicht, H. P. *J. Prakt. Chem.* **1970**, *312*, 456.

(16) Cullen, W. R.; Dawson, D. S. *Can. J. Chem.* **1967**, *45*, 2889.

(17) Alt, H. G.; Engelhardt, H. E.; Steinlein, E. *J. Organomet. Chem.* **1988**, *344*, 227.

(18) Shih, K.; Tylicki, R. M.; Wu, W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1995**, *229*, 105.

(19) Hoffman, D. M.; Huffman, J. C.; Lappas, D.; Wierda, D. A. *Organometallics* **1993**, *12*, 4312.

(20) Hughes, D. L.; Marjani, K.; Richards, R. L. *J. Organomet. Chem.* **1995**, *505*, 127.

(21) Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1994**, *13*, 3767.

(22) Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1994**, *13*, 3788.

(23) James, B. R.; Mahajan, D. *Can. J. Chem.* **1979**, *57*, 180.

(24) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

(25) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(26) Rottink, M. K.; Angelici, R. J. *Inorg. Chem.* **1993**, *32*, 2421.

(27) Angelici, R. *Acc. Chem. Res.* **1995**, *28*, 51.

(28) Burn, M. J.; Kiel, G.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850.

(29) Takats, J. *Polyhedron* **1988**, *7*, 931.

(30) Wong, W.; Singer, S. J.; Pitts, W. D.; Watkins, S. F.; Baddley, W. H. *J. Chem. Soc., Chem. Commun.* **1972**, 672.

(31) Padolik, L. L.; Gallucci, J.; Wojcicki, A. *J. Organomet. Chem.* **1990**, *383*, C1.

(32) Davidson, J. L.; Shiralian, M. *J. Chem. Soc., Dalton Trans.* **1984**, 2167.

(33) Kiel, G.; Takats, J. *Organometallics* **1989**, *8*, 839.

(34) Keiter, R. L.; Rheingold, A. L.; Hamerski, J.; Castle, C. *Organometallics* **1983**, *2*, 1635.

(35) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press Inc.: New York, 1981, pp 151-182.

(36) Sheridan, J. B.; Johnson, J. R.; Handwerker, B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2404.

(37) Collin, J. *Bull. Soc. Chim. Fr.* **1988**, 976.

(38) Chen, J.; Sen, A. *J. Am. Chem.Soc.* **1984**, *106*, 1506.

(39) Grevels, F.; Buchkremer, J.; Koerner Von Gustorf, E. A. *J. Organomet. Chem.* **1976**, *111*, 325.

(40) Liebeskind, L. S.; Baysdon, S. L.; South, M. S.; Iyer, S.; Leeds, J. P. *Tetrahedron* **1985**, *41*, 5839.

(41) Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25.

(42) Washington, J. Ph. D. Thesis, University of Alberta, 1994.

(43) Baird, M. C.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. (A)* **1967**, 1347.

(44) Brix, H.; Beck, W. *J. Organomet. Chem.* **1982**, *234*, 151.

(45) Reger, D. L.; Mintz, E. *Organometallics* **1984**, *3*, 1759.

(46) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 3728.

(47) Andersen, J.; Moss, J. R. *Organometallics* **1994**, *13*, 5013.

(48) Hoberg, H.; Herrera, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 876.

(49) Kang, J. W.; McVey, S.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3189.

(50) Corrigan, P. A.; Dickson, R. S. *Aust. J. Chem.* **1979**, *32*, 2147.

(51) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771.

(52) Cooke, R. B. M.; Green, M. *J. Chem. Soc. (A)* **1970**, 2981.

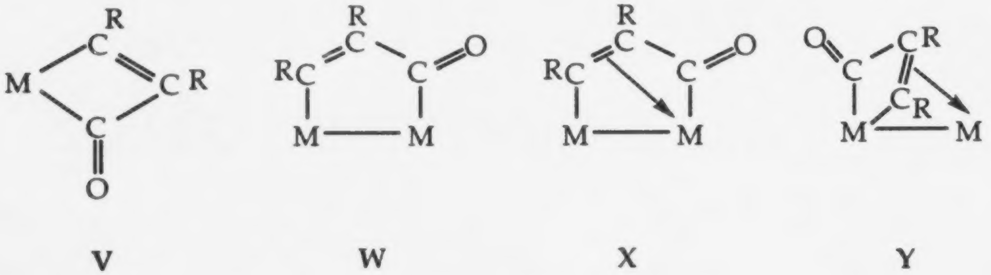
(53) Padolik, L. L.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 9986.

Chapter 4

The Role of Metallacyclobutenone in the Formation of Dimetallacyclopentenone Complexes

4.1 Introduction

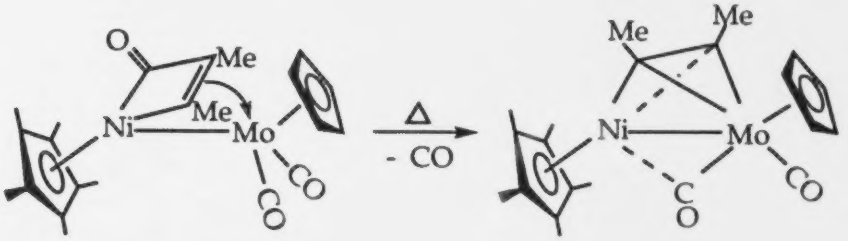
Coupling reactions between carbon monoxide and alkynes promoted by transition-metal carbonyl complexes have attracted much attention for almost five decades.[1] A wide variety of new organic ligands[2-6] and organic compounds[7,8] have been synthesized. It has been proposed that metallacyclobutenones (V) and dimetallacycles (W), (X) and (Y) are probable intermediates in these reactions (Scheme 4.1).



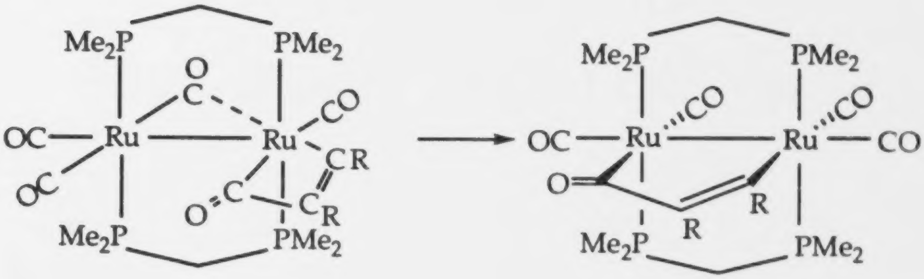
Scheme 4.1

Although there are a number of examples of metallacyclobutenone complexes (V)[9-14] and dimetallacycles (W),[2,15-19] (X),[2-4,16,20-22] and (Y)[23-28] reported in the literature, studies on the relationship between these species are very limited. Recently, Chetcuti reported that species of the type Y can be converted to a dimetallatetrahedrane by heating (eq. 4.1),[26,27] and

Gladfelter showed that ring expansion of the dinuclear ruthenacyclobutenone species gives the diruthenacyclopentenone complex (eq. 4.2).[19] These studies prompted us to investigate possible ring expansion of osmacyclobutenones that had been prepared. Compound **10a** was chosen as it also contains a chelating dppm ligand. Complexes containing a dppm ligand are well known to be versatile building blocks for the synthesis of dinuclear complexes.[21,22,29-31] Thus, the reaction of **10a** with $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ and $CpRh(CO)_2$, was undertaken. The results of this study are reported in this Chapter.


O
Me
Me
Ni
Mo
CO
CO
Δ
- CO
Me
Me
Ni
Mo
C
O
CO

(4.1)


Me2P
PMe2
O
C
CO
OC
Ru
Ru
CR
OC
O=C
CR
Me2P
PMe2
Me2P
PMe2
CO
CO
OC
Ru
Ru
CO
O=
R
R
Me2P
PMe2

(4.2)

R = CO_2Me

4.2. Results and Discussion

4.2.1. Reaction of $\text{Os(CO)}_2\{\eta^2\text{-C}_2\text{H}_2\text{C(O)}\}(\eta^2\text{-dppm})$ (10a) with $\text{Ru(CO)}_4(\eta^2\text{-C}_2\text{H}_4)$

Reaction of compound **10a** with $\text{Ru(CO)}_4(\eta^2\text{-C}_2\text{H}_4)$ afforded the dinuclear complex $\text{OsRu(CO)}_5(\text{C}_2\text{H}_2\text{CO})(\text{dppm})$ (**13**) in good yield (eq. 4.3).

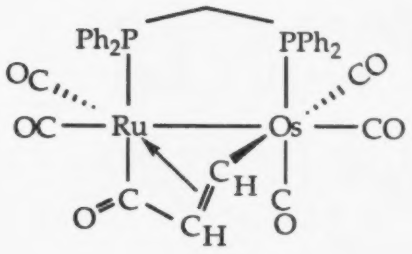
$$\mathbf{10a} \xrightarrow[\text{CH}_2\text{Cl}_2/\text{pentane}]{+\ \text{Ru(CO)}_4(\eta^2\text{-C}_2\text{H}_4)} \underset{\mathbf{13}}{\text{OsRu(CO)}_5(\text{C}_2\text{H}_2\text{CO})(\text{dppm})} \quad (4.3)$$

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two signals at δ 30.8 and 8.4, the lower field positions compared to those of **10a** indicate the formation of a five-membered ring, consistent with the presence of a bridging dppm unit.[32,33] Moreover, the chemical shift of δ 30.8 is similar to those found in $\text{Ru}_2(\text{CO})_5(\mu\text{-C}_2\text{H}_2\text{CO})(\mu\text{-dppm})$ (δ 30.3 and 44.2)[20] and $\text{Ru}_2(\text{CO})_4(\mu\text{-C}_2\text{H}_2\text{CO})(\mu\text{-dppm})_2$ (δ 27.7 and 30.0).[17] and is assigned to the ruthenium coordinated end of the μ-dppm ligand whereas the signal at δ 8.4 is attributed to the one attached to osmium. The IR spectrum showed five terminal carbonyl bands and one band at 1707 cm^{-1}. The position of the latter band is typical of an acyl group in a dimetallacyclopentenone ring in which the double bond is also coordinated to a metal center (Table 4.1).[2,3,20,34-36] In the case of dimetallacyclopentenones without double bond coordination, the band will shift to lower frequency.

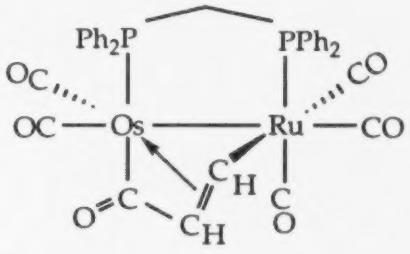
Table 4.1: IR Data for 13 and Related Compounds

Compound	ν(acyl) (cm^{-1}, CH_2Cl_2)
$OsRu(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (**13**)	1707
$Ru_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$[20]	1703
$Fe_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$[35]	1725
$OsRhCp(CO)_4\{\mu\text{-}C_2H_2C(O)\}$[36]	1738
$OsRhCp(CO)_3(PMe_2Ph)\{\mu\text{-}C_2H_2C(O)\}$[37]	1696

On the basis of the previously synthesized $Ru_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ complex,[20] two possible structures, with different orientations of the $\{C_2H_2C(O)\}$ bridge are possible, one having the acyl bound to the ruthenium center (**Z**), and the other having the acyl bound to the osmium center (**Z'**).



Z



Z'

The ^1H NMR spectrum showed four resonances at δ 8.1, 5.43, 4.53, and 2.82, each integrating as one proton. The low field signals at δ 8.1 and 5.43 are characteristic of the protons of the $C(H_\beta)=C(H_\alpha)C(O)$ group with alkene moiety coordinated to a metal center (Table 4.2). The two resonances at δ 4.53 and 2.82 are assigned to the methylene protons of dppm, although the large separation between the two signals is noteworthy. Selective ^{31}P decoupling experiments showed that the β hydrogen is associated with the Os-bound phosphine, as decoupling the ^{31}P resonance at δ 8.4 led to collapse of the doublet of doublets at δ 8.1 into a doublet, while decoupling the other ^{31}P resonance had no effect. On the other hand, the α hydrogen resonance, which is a doublet of doublets, collapsed into a doublet on selectively decoupling the ^{31}P resonance at δ 30.8, and remained unchanged upon decoupling the other ^{31}P resonance. The presence of strong coupling (15.3 Hz) between the α hydrogen and the Ru-bound phosphine is in better agreement with structure **Z** than **Z'**, as the latter **Z'** involves a four-bond coupling between the α proton and the Ru-bound phosphine, which is usually quite small.[17,20,38]

Table 4.2: Selected ^1H NMR Data for 13 and Related Compounds

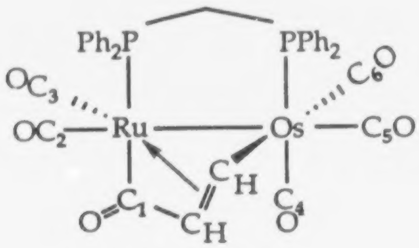
Compound	δ (ppm, CD_2Cl_2)		
	H_α	H_β	$^3J_{HH}$ (Hz)
$OsRu(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (**13**)	5.43	8.1	8.2
$Ru_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$[20]	4.61	8.22	8.5
$Fe_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$[35]	3.63	8.63	7
$OsRhCp(CO)_4\{\mu\text{-}C_2H_2C(O)\}$[36]	5.00	7.85	7.4
$OsRhCp(CO)_3(PMe_2Ph)\{\mu\text{-}C_2H_2C(O)\}$[37]	4.72	8.82	6.3

The $^{13}C\{^1H\}$ NMR spectrum (Figure 4.1) shows a low field doublet at δ 233.3 ($^2J_{CP}$ = 59.4 Hz), which is assigned to the acyl group. The large coupling constant indicates that the acyl moiety is *trans* to a phosphorus atom. The resonances at δ 205.0 and 200.3 ($^2J_{CP}$ = 11.06 Hz) are typical of the terminal carbonyls that are bound to ruthenium, whereas the resonances at δ 185.0 ($^2J_{CP}$ = 10.06 Hz), 180.3 ($^2J_{CP}$ = 97.6 Hz, $^3J_{CP}$ = 6.03 Hz), and 178.0 ($^2J_{CP}$ = 10.06 Hz) are characteristic of terminal osmium carbonyls.[39] The large coupling indicates that the carbonyl at δ 180.3 is *trans* to a phosphine and consequently assigned to CO(4) in the diagram appearing in Figure 4.1. The signals at δ 200.3 and 178.0 are attributed to carbonyl ligands labelled CO(2) and CO(5), respectively. In a related compound, $RuOs(CO)_6\{\mu\text{-}\eta^1{:}\eta^1\text{-}C_2H_2)\}(\mu\text{-dppm})$ (**15**) that will be described in Chapter 5, it is clearly demonstrated that a carbonyl ligands *trans* to a metal-metal bond are located at high field. Pomeroy has also reported that carbonyl ligands *trans* to a dative metal-metal bond are usually found at high field.[40-43] The remaining resonances, not shown in the Figure, at δ 141.1 and 55.0 are attributed to the alkene carbons in the CHCHC(O) group (Table 4.3); as expected these signals appear as doublets in the ^1H coupled spectrum (δ 141.1, $^1J_{CH}$ = 143.4 Hz and 55.0, $^1J_{CH}$ = 161.5 Hz) . The coupling constants

Table 4.3: Selected $^{13}C\{^1H\}$ NMR Data for 13 and Related Compounds

Compound	δ (ppm, CD_2Cl_2)	
	C_α	C_β
$OsRu(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (**13**)	55.0	141.1
$Ru_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$[20]	55.4	161.9
$Fe_2(CO)_5\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$[35]	44.8	168.4
$OsRhC_p(CO)_4\{\mu\text{-}C_2H_2C(O)\}$[36]	44.4	115.7
$OsRhC_p(CO)_3(PMe_2Ph)\{\mu\text{-}C_2H_2C(O)\}$[37]	52.8	156.0

are similar to that of ethylene (156 Hz).[44] Furthermore, an APT experiment is in accord with these assignments. Thus, the IR and NMR data are in accord with structure **Z** for compound **13**. This formulation has also been confirmed by an X-ray structure determination.[45]


Ph2P
PPh2
OC3
C6O
OC2
Ru
Os
C5O
C
H
C4
O
O
C1
CH

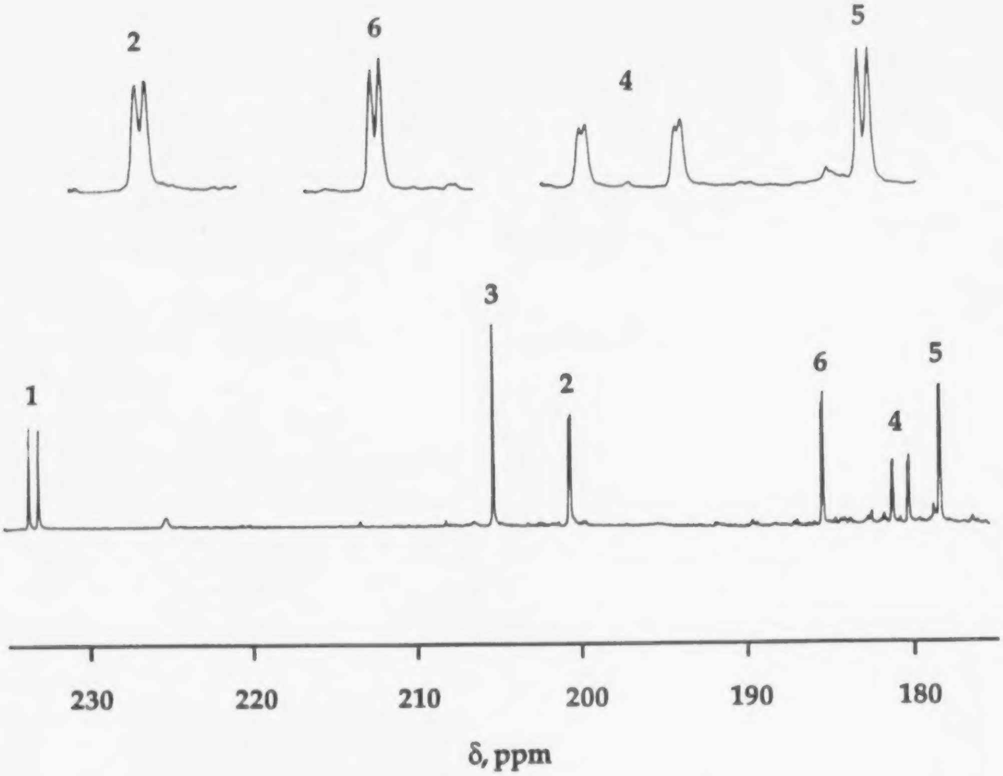
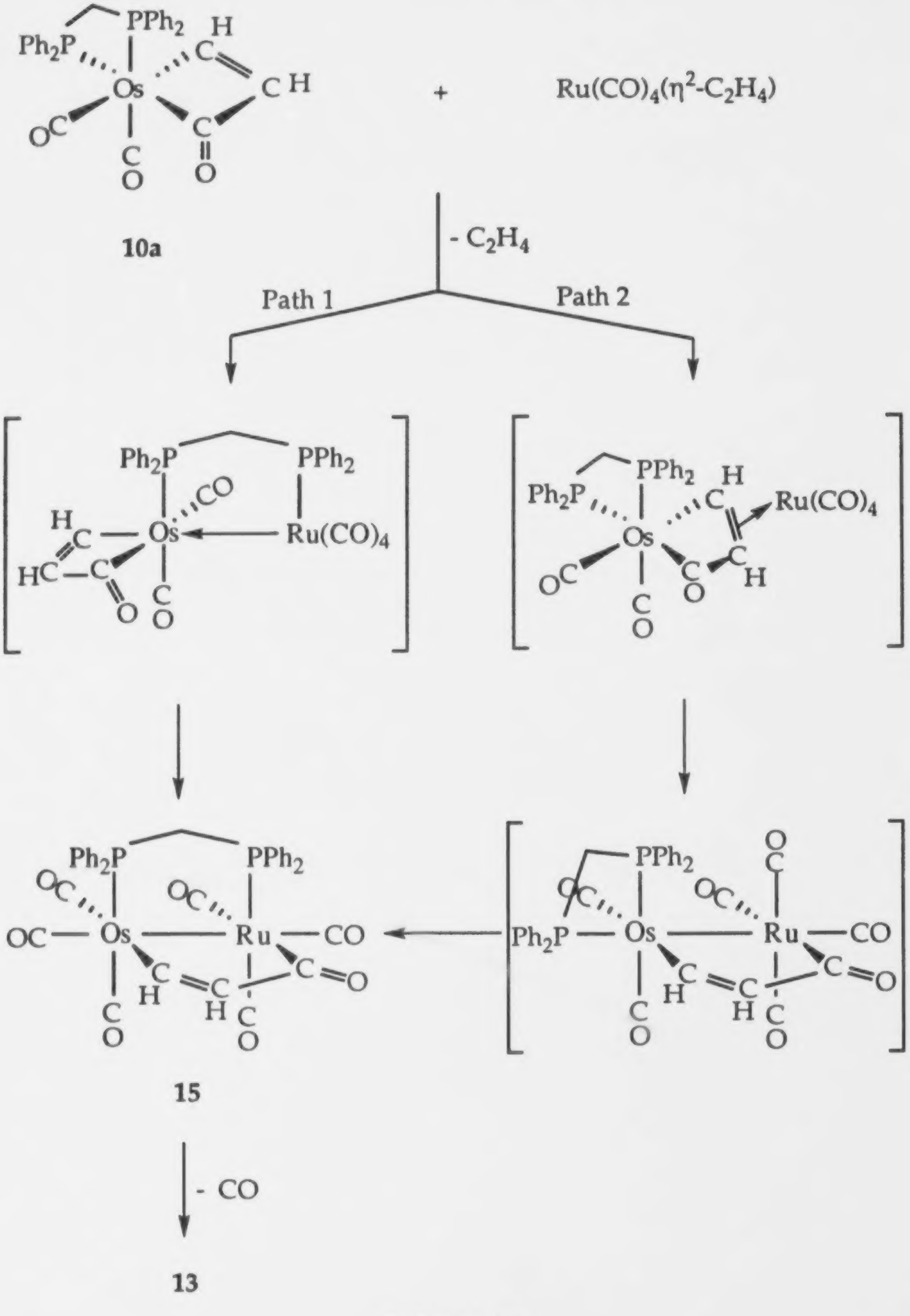


Figure 4.1: $^{13}C\{^1H\}$ NMR Spectrum of 13 in the Carbonyl Region (Below); Expansion of Some of the Signals (Top).

Formation of compound 13. In an attempt to gain some information about intermediates in the formation of **13**, the reaction of compound **10a** with $Ru(CO)_4(\eta^2-C_2H_4)$ was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. From - 80°C to - 10°C, no new species except the starting materials were observed. At 0°C, both ^1H and $^{31}P\{^1H\}$ NMR spectra showed a new species **15**. The ^1H NMR spectrum of **15** showed two resonances at δ 8.19 and 7.72, characteristic of the $\{CH=CHC(O)\}$ protons of a dimetallacyclopentenone ring.[16,17] Upon warming the solution to room temperature, this species gradually converted to the final product **13**. No other species was observed. Full characterization of compound **15** and its transformation to compound **13** will be discussed in Chapter 5.

The lability of ethylene ligand in $Ru(CO)_4(\eta^2-C_2H_4)$ is well documented.[20,46-49] After ethylene dissociation, there are two possible intermediates that might form (Scheme 4.1); one is through phosphine coordination (Path 1), the other is through alkene group coordination (Path 2). Further transformations in both pathways require opening of the two four-membered rings of **10a**. Opening of a four-membered ring containing the dppm ligand to generate a dangling phosphine is well documented.[21,22,29,30] Ring expansion of a metallacyclobutenone ring to a dimetallacyclopentenone ring is, however, very rare. As a matter of fact, to the best of our knowledge, there is only one recent study by Gladfelter which demonstrated ring expansion of a ruthenacyclobutenone species to a diruthenacyclopentenone at room temperature.[19] Our failure to observe the first intermediate in Path 1 may be rationalized in terms of its slow formation and rapid conversion to **15**. In a related mechanistic study of $Ru(CO)_4(\eta^1\text{-dppm})$ with $Os(CO)_4(\eta^2-C_2H_2)$ (Chapter 5), it has been found


10a
+
Ru(CO)$_4$(η^2-C$_2$H$_4$)
- C$_2$H$_4$
Path 1
Path 2
Ru(CO)$_4$
15
- CO
13

Scheme 4.2

that the same intermediate is readily converted to the intermediate **15**. Although the initial step of Path 2 is favorable due to the coordination of the better π-acidic alkene moiety of **10a** and its high concentration compared to the ring opened $Os(CO)_2(\eta^2\text{-}C_2H_2CO)(\eta^1\text{-dppm})$ required in Path 1, the last step may be slow because it involves both ring opens and ligand rearrangement. Therefore, both pathways are possible.

4.2.2. Reaction of $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (10a) with $CpRh(CO)_2$

Compound **10a** reacted with $CpRh(CO)_2$ in toluene, but only at reflux temperature, to give complex **14** in 80% yield (4.4).

$$\mathbf{10a} + CpRh(CO)_2 \xrightarrow[110°C]{\text{toluene}} \underset{\mathbf{14}}{CpRhOs(CO)_3(C_2H_2CO)(dppm)} \quad (4.4)$$

The mass spectrum and elemental analysis of compound **14** agreed with the formulation as shown in eq. 4.2. The IR spectrum of **14** showed three terminal carbonyl bands and one band at 1588 cm^{-1}, which is attributed to the acyl group in the {CH=CHC(O)} group. The low energy band at around 1600 cm^{-1} implies that the alkene group is not coordinated to the metal center (Table 4.4).

In the $^{31}P\{^1H\}$ NMR spectrum two resonances were observed at δ 44.6 ($^1J_{RhP}$ = 186 Hz, $^2J_{PP}$ = 62.4 Hz) and - 21.3 ($^2J_{PP}$ = 62.4 Hz). The signal at δ 44.6 is assigned to the phosphine that is coordinated to the rhodium center due to the strong coupling observed between rhodium and phosphorus, the other signal at δ -21.3 is attributed to the osmium coordinated phosphine.

Table 4.4: IR Data for 14 and Related Compounds

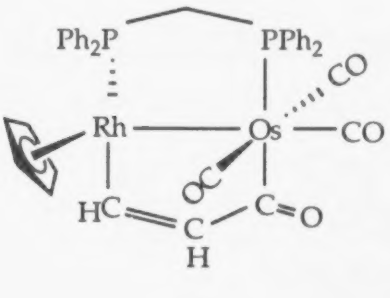
Compound	υ(acyl) (cm-1)
$OsRhCp(CO)_3\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (13)	1588[a]
$OsIrCp(CO)_5\{\mu\text{-}C_2H_2C(O)\}$[36]	1598[a]
$OsRu(CO)_8\{\mu\text{-}C_2H_2C(O)\}$[16]	1635[b]
$Rh_2(Cp)_2(CO)_2\{\mu\text{-}C_2(CF_3)_2C(O)\}$[50]	1628[b]

[a]In CH_2Cl_2. [b]In pentane.

In the ^1H NMR spectrum two doublets at δ 7.93 and 5.31, in a ratio of 1:5, are assigned to the β proton of the $\{CH_\beta CH_\alpha C(O)\}$ group and the C_5H_5 group while the α proton of the $\{CH_\beta CH_\alpha C(O)\}$ group is hidden in the phenyl region.[16,17] The remaining two resonances at δ 4.70 and 4.15 are characteristic of the methylene protons of the dppm ligand. The $^{13}C\{^1H\}$ NMR spectrum showed four equal-intensity resonances at δ 188.9 ($^2J_{CP_{Os}}$ = 94 Hz), 184.4 ($^2J_{CP_{Os}}$ = 8 Hz), 170.8 ($^2J_{CP_{Os}}$ = 9 Hz), and a singlet at δ 161.4. Heteronuclear $^{13}C\{^{31}P\}$ decoupling experiments clearly established that the coupling is due to phosphorus only and that the carbonyls are coupled to the phosphorus that is coordinated to the osmium center. The signal at δ 188.9 is assigned to the acyl group. The large coupling constant ($^2J_{CP_{Os}}$ = 94 Hz) between the acyl and the phosphorus indicates that they are *trans* to each other. The other signals at δ 184.4, 170.8, and 161.4 are due to the terminal carbonyls. The small couplings between these carbonyls and the phosphorus suggest that they are oriented *cis* to the phosphine. The resonances at δ 163.3 ($^1J_{RhC}$ = 6.6 Hz) and 150.3 ($^3J_{CP_{Os}}$ = 16 Hz) are assigned to the β and α carbons of the $\{C_\beta HC_\alpha HC(O)\}$ group (Table 4.5).[16,17] The remaining resonances at δ 93.2 and 39.3 are attributed to the C_5H_5 group and the methylene of dppm. In the ^1H coupled spectrum, the resonances at δ 188.9 ($^2J_{CH}$ = 4.5 Hz, acyl),[51] 163.3 ($^1J_{CH}$ = 145.4 Hz, CHCHC(O)),[44] 150.3 ($^1J_{CH}$ = 143.3 Hz, CHCHC(O)),[44] 93.2 ($^1J_{CH}$ = 175.0 Hz, C_5H_5)[44] showed additional doublet splitting, which is consistent with the assignments; the signal at δ 39.3 was too weak due to its complicated coupling to both phosphorus atoms and the methylene protons. Furthermore, an APT experiment also agreed with the assignments. Thus the proposed structure of compound **14** is as shown below.

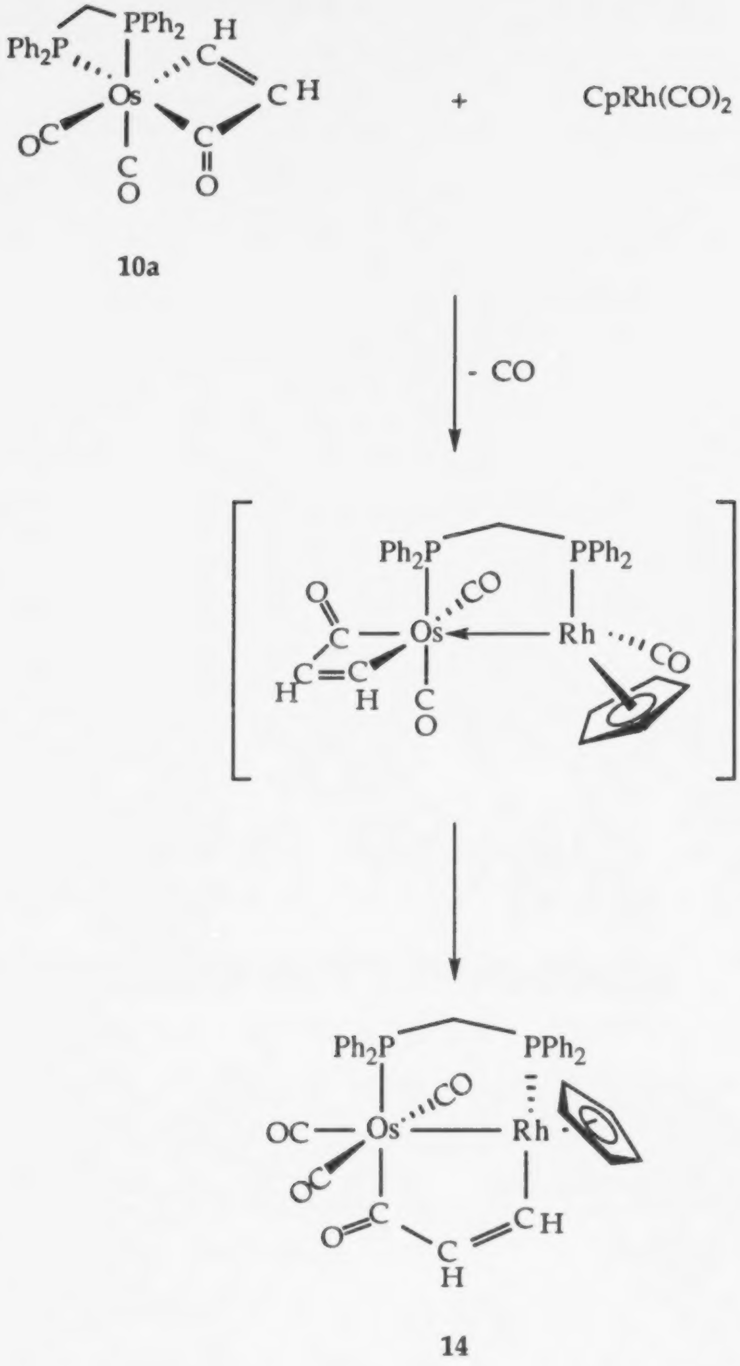
Table 4.5: Selected $^{13}C\{^1H\}$ NMR Data for 14 and Related Compounds

Compound	δ (ppm, CD_2Cl_2)	
	C_α	C_β
$OsRhC_p(CO)_3\{\mu\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (**14**)	150.3	163.3
$OsRu(CO)_8\{\mu\text{-}C_2H_2C(O)\}$[16]	131.4	166.5
$Ru_2(CO)_4(\mu\text{-}C_2H_2C(O))(\mu\text{-dppm})_2$[17]	170.8	176.8



14

Formation of 14. In light of the mechanistic investigation into the formation of compound **13**, a similar mechanism is proposed for compound **14** (Scheme 4.2).


10a
CpRh(CO)2
- CO
14

Scheme 4.3

Consistent with initial CO dissociation from $CpRh(CO)_2$,[52,53] the reaction does not take place at room temperature and elevated temperatures are required. In a related study, the reaction of compound **10a** with $(C_5Me_5)Ir(CO)_2$ was performed in refluxing toluene. This reaction took much longer (53 h) than with $CpRh(CO)_2$, which is in accord with reduced lability of the carbonyl ligands in $(C_5Me_5)Ir(CO)_2$. However separation and isolation of the products were not successful.

It is notable that in **14** the acyl ligand remains on osmium whereas in **13** it has migrated from osmium to ruthenium; at present we have no rational explaination for these differences.

4.3. Conclusions

The reactions of $Os(CO)_2(\eta^2-C_2H_2CO)(\eta^2-dppm)$ (**10a**) with $Ru(CO)_4(\eta^2-C_2H_4)$ and $CpRh(CO)_2$ have been shown to generate dimetallacyclopentenone complexes. In the case of the reaction of $Ru(CO)_4(\eta^2-C_2H_4)$, low temperature NMR studies established that the dimetallacyclopentenone species **13** is derived from ring expansion of the osmacyclobutenone precursor. This is important since it implies that a metallacyclobutenone may play a role in the formation of dimetallacyclopentenones.

4.4. Experimental Section

4.4.1. Starting Materials and Reagents

$Ru(CO)_4(\eta^2\text{-}C_2H_2)$[46] and $CpRh(CO)_2$[54] were prepared by published procedures.

4.4.2. Synthetic Procedures

Synthesis of $OsRu(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}CHCHC(O)\}(\mu\text{-dppm})$, 13

A yellow solution of $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (**10a**) (50 mg, 0.0731 mmol) in 15 mL CH_2Cl_2 was added to a colorless solution of $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ (17.7 mg, 0.0734 mmol) in 13 mL pentane at - 78°C. The mixture was allowed to slowly warm to room temperature and stirring was maintained at room temperature for 5 h. The solvent was then removed in vacuo. The orange residue was recrystallized from CH_2Cl_2/pentane to give 44 mg (69%) of compound **13**. Anal Calcd. for $C_{33}H_{24}O_6OsP_2Ru$: C, 45.57; H, 2.78. Found: C, 45.66; H, 2.44.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2061 s, 2002 sh, 1990 vs, 1966s, 1945 sh; υ_{acyl}: 1707 w.

^1H NMR: 8.1 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{P_{Os}H}$ = 15.5 Hz, 1H), 5.43 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{P_{Ru}H}$ = 15.3 Hz, 1H), 4.53 (dm, $^2J_{HH}$ = 13.7 Hz, $^2J_{P_{Os}H}$ = 10.6 Hz, $^2J_{P_{Ru}H}$ = 9.7 Hz, 1H), 2.82 (dm, $^2J_{HH}$ = 13.7 Hz, $^2J_{P_{Os}H}$ = 11.2 Hz, $^2J_{P_{Ru}H}$ = 10.0 Hz, 1H).

$^{31}P\{^1H\}$ NMR: 30.8 (d, $^2J_{PP}$ = 120 Hz, P-Ru), 8.4 (d, $^2J_{PP}$ = 120 Hz, P-Os).

$^{13}C\{^1H\}$ NMR: 233.2 (d, $^2J_{CP}$ = 59.4 Hz, acyl), 205.0 (s, 1CO), 200.3 (d, $^2J_{CP}$ = 11.06 Hz, 1CO), 185.0 (d, $^2J_{CP}$ = 10.06 Hz, 1CO), 180.3 (dd, $^2J_{CP}$ = 97.60 Hz, $^3J_{PC}$ = 6.03 Hz, 1CO), 178.0 (d, $^2J_{CP}$ = 10.06 Hz, 1CO), 141.1 (dd, J_{CP} = 9.4 Hz, $^1J_{CH}$ =

143.4 Hz, $C_{\beta}H$), 55.0 (dd, J_{CP} = 14.9 Hz, $^1J_{CH}$ = 161.5 Hz, $C_{\alpha}H$), 41.3 (dd, $^1J_{CP}$ = 32.5 Hz, $^1J_{CP}$ = 12.8 Hz, $PPh_2CH_2PPh_2$)

Synthesis of $CpRhOs(CO)_3\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}CHCHC(O)\}(\mu\text{-}dppm)$, 14

A pale orange solution of $CpRh(CO)_2$ (23.2 mg, 0.104 mmol) in 10 mL toluene was added to a suspension of $Os(CO)_2(\eta^1,\eta^1\text{-}C(O)C_2H_2)(\eta^2\text{-}dppm)$ (71 mg, 0.104 mmol) in 10 mL toluene. The yellow suspension was then heated to 110°C, during which time the yellow suspension gradually changed to an orange solution. The solution was kept refluxing for 4 h before it was cooled to ambient temperature. The solvent was removed in vacuo. After recrystallization from CH_2Cl_2/pentane, compound **14** was obtained as a yellow solid (74 mg, 80%). Anal Calcd. for $C_{36}H_{29}O_4OsP_2Rh\cdot CH_2Cl_2$: C, 46.02; H, 3.24. Found: C, 46.00; H, 2.80. One equivalent of CH_2Cl_2 was verified by ^1H NMR in d_8-THF. MS (Fab): M^+ - n CO, n = 0-3; loss of COC_2H_2 was observed also.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2038 s, 1978 s, 1949 s; υ_{acyl}: 1588 w.

^1H NMR: 7.93 (dd, $^3J_{HH}$ = 9.3 Hz, $^3J_{P_{Os}H}$ = 3.3 Hz, 1H), 5.31 (d, $^4J_{P_{Rh}H}$ = 1.4 Hz, 5H), 4.70 (m, $^2J_{HH}$ = 13.2 Hz, $^2J_{RhH}$ = 6.8 Hz, $^2J_{P_{Rh}H}$ = 9.8 Hz, $^2J_{P_{Os}H}$ = 10.6 Hz, 1H), 4.15 (dt, $^2J_{HH}$ = $^2J_{P_{Os}H}$ = 13.2 Hz, $^2J_{P_{Rh}H}$ = 12.4 Hz, 1H).

$^{31}P\{^1H\}$ NMR: 44.6 (dd, $^2J_{PP}$ = 62.4 Hz, $^1J_{RhP}$ = 186 Hz, P-Rh), - 21.3 (d, $^2J_{PP}$ = 62.4 Hz, P-Os).

$^{13}C\{^1H\}$ NMR: 188.9 (d, $^2J_{P_{Os}C}$ = 94 Hz, acyl), 184.4 (d, $^2J_{P_{Os}C}$ = 8 Hz, 1CO), 170.8 (d, $^2J_{P_{Os}C}$ = 9 Hz, 1CO), 163.3 (d, $^1J_{RhC}$ = 6.6 Hz, Rh-C(H)=), 161.4 (s, 1CO), 150.3 (d, $^3J_{P_{Os}C}$ = 16 Hz, Os-C(O)-C(H)=), 93.2 (s, Cp), 39.3 (ddd, $^1J_{PC}$ = 36.7 Hz, $^1J_{PC}$ = 28.6 Hz, $^2J_{RhC}$ = 4.3 Hz, $PPh_2CH_2PPh_2$).

Characterization of $OsRu(CO)_6\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}CHCHC(O)\}(\mu\text{-dppm})$, 15

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2071 s, 2035 s, 2002 s, 1989 sh, 1960 m; υ_{acyl}: 1605 w.

^1H NMR (0°C): 8.19 (dd, $^3J_{HH} = 9.60$ Hz, $^3J_{P_{Os}H} = 2.04$ Hz, 1H), 7.72 (dd, $^3J_{HH} = 9.60$ Hz, $^4J_{P_{Os}H} = 4.08$ Hz, 1H), 4.90 (dt, $^2J_{HH} = 14.20$ Hz, $^2J_{P_{Os}H} = 10.83$ Hz, $^2J_{P_{Ru}H} = 10.92$ Hz, 1H), 4.43 (m, $^2J_{HH} = 14.20$ Hz, $^2J_{P_{Os}H} = 13.39$ Hz, $^2J_{P_{Ru}H} = 11.40$ Hz, 1H).

$^{31}P\{^1H\}$ NMR (0°C): 20.9 (d, $^2J_{PP} = 68.2$ Hz, P-Ru), - 16.7 (d, $^2J_{PP} = 68.2$ Hz, P-Os).

$^{13}C\{^1H\}$ NMR (- 40°C): 250.7 (dd, $^2J_{acyl\text{-}CO} = 21.0$ Hz, $^2J_{P_{Ru}C} = 11.1$ Hz, acyl), 201.6 (d, $^2J_{P_{Ru}C} = 89.5$ Hz, 1CO), 199.6 (m, $^2J_{acyl\text{-}CO} = 21.0$ Hz, $^2J_{P_{Ru}\text{-}C} = 10.2$ Hz, 1CO), 188.8 (d, $^2J_{P_{Ru}C} = 13.1$ Hz, 1CO), 185.9 (d, $^2J_{P_{Os}C} = 92.6$ Hz, 1CO), 183.6 (d, $^2J_{P_{Os}C} = 8.0$ Hz, 1CO), 172.0 (d, $^2J_{P_{Os}C} = 9.1$ Hz, 1CO).

4.5. References

(1) Pino, P.; Braca, G. In *Organic Syntheses via Metal Carbonyls;* I. Wender and P. Pino, Ed.; Wiley-Interscience: New York, 1977; Vol. 2; pp 419-516.

(2) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

(3) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1988**, 358.

(4) Takats, J. *J. Cluster Sci.* **1992**, *3*, 479.

(5) Washington, J.; McDonald, R.; Takats, J.; Menashe, N.; Reshef, D.; Shvo, Y. *Organometallics* **1995**, *14*, 3996.

(6) Dickson, R. S. *Polyhedron* **1991**, *10*, 1995.

(7) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation. Direct Synthesis of Carbonyl Compounds;* Plenum Press: New York, 1991.

(8) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

(9) Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. (A)* **1970**, 2981.

(10) Padolik, L. L.; Callucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 9986.

(11) Padolik, L. L.; Gallucci, J.; Wojcicki, A. *J. Organomet. Chem.* **1990**, *383*, C1.

(12) Wong, W.; Singer, S. J.; Pitts, W. D.; Watkins, S. F.; Baddley, W. H. *J. Chem. Soc., Chem. Commun.* **1972**, 672.

(13) Corrigan, P. A.; Dickson, R. S.; Fallon, G. D.; Michel, L. J.; Mok, L. *Aust. J. Chem.* **1978**, *31*, 1937.

(14) Corrigan, P. A.; Dickson, R. S. *Aust. J. Chem.* **1979**, *32*, 2147.

(15) Knox, S. A. R. *Pure Appl. Chem.* **1984**, *56*, 81.

(16) Burn, M. J.; Kiel, G.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850.

(17) Mirza, H. A.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1994**, *13*, 3063.

(18) Jonson, K. A.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1991**, *113*, 5097.

(19) Johnson, K. A.; Gladfelter, W. *Organometallics* **1992**, *11*, 2534.

(20) Kiel, G.; Takats, J. *Organometallics* **1989**, *8*, 839.

(21) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1987**, 662.

(22) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 741.

(23) Boag, N. M.; Goodfellow, R. J.; Green, M.; Hessner, B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2585.

(24) Azar, M. C.; Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 7209.

(25) Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *Organometallics* **1987**, *6*, 2298.

(26) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1995**, *14*, 2937.

(27) Chetcuti, M. J.; Green, K. A. *Organometallics* **1988**, *7*, 2450.

(28) Chetcuti, M. J.; Grant, B. E. *J. Am. Chem. Soc.* **1989**, *111*, 2743.

(29) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(30) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.

(31) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1185.

(32) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(33) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

(34) Hogarth, G.; Knox, S. A. R.; Lloyd, B. R.; MacPherson, K. A.; Morton, D. A. V.; Orpen, A. G.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1988**, 360.

(35) Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L.; Hogarth, G. *Polyhedron* **1995**, *14*, 2723.

(36) Washington, J. Ph. D. Thesis, University of Alberta, 1994.

(37) Takats, J.; Washington, J.; Santarsiero, B. *Organometallics* **1994**, *13*, 1078.

(38) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 741.

(39) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press Inc.: New York, 1981, pp 151-182.

(40) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854.

(41) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *4*, 250.

(42) Einstein, F. W. B.; Johnston, V. J.; Ma, A. K.; Pomeroy, R. K. *Organometallics* **1990**, *9*, 52.

(43) Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1991**, *10*, 3620.

(44) Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley-Interscience, John Wiley & Sons, Inc.: New York, 1972, pp 28-29.

(45) Day, V., Personal communication.

(46) Johnson, B. F. G.; Lewis, J.; Twigg, M. V. *J. Organomet. Chem.* **1974,** *67*, C75.

(47) Linder, E.; Jansen, R.; Mayer, H. A.; Hiller, W.; Fawzi, R. *Organometallics* **1989,** *8*, 2355.

(48) Sandercock, P. M. M.Sc. Thesis, University of Alberta, 1990.

(49) Hoffman, K. C. M. Sc. Thesis, University of Alberta, 1994.

(50) Dickson, R. S.; Gatehouse, B. M.; Nesbit, M. C.; Pain, G. N. *J. Organomet. Chem.* **1981,** *251*, 97.

(51) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1991, pp 247-248.

(52) Schuster-Waldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966,** *88*, 1657.

(53) Vest, P.; Anhaust, J.; Bajaj, H. C.; van Eldik, R. *Organometallics* **1991,** *10*, 818.

(54) Dickson, R. S.; Tailby, G. R. *Aust. J. Chem.* **1970,** *23*, 1531.

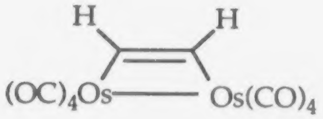
Chapter 5

Reaction of $M(CO)_4(\eta^2\text{-alkyne})$ with $M'(CO)_4(\eta^1\text{-dppm})$

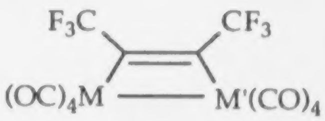
$(M, M' = Ru, Os)$

5.1 Introduction

Recent work from our laboratories has demonstrated that the 18-electron $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) complexes undergo facile condensation reactions with other 18-electron compounds, such as $M(CO)_5$ (M = Ru, Os) and $(C_5R_5)M''(CO)_2$ (M'' = Co, Rh, Ir) to generate dimetallacyclic complexes. A variety of dimetallacycles (A', B', C', and D') have been obtained depending on both the metal and the alkyne employed.[1-3]

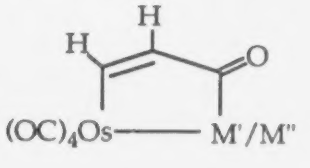

H
H
(OC)4Os
Os(CO)4

A'


F3C
CF3
(OC)4M
M'(CO)4

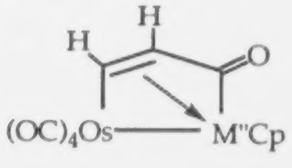
M, M' = Ru, Os

B'


H
H
O
(OC)4Os
M'/M''

M' = Ru(CO)$_4$; M'' = CpIr(CO)

C'


H
H
O
(OC)4Os
M''Cp

M'' = Co, Rh

D'

Attempts to observe reaction intermediates by NMR monitoring the reactions were largely unsuccessful.[4] In previous Chapters it was shown that reaction of $M(CO)_4(\eta^2\text{-alkyne})$ complexes with phosphines yields, besides simple substitution, CO inserted products. This suggested that similar chemistry with $M(CO)_4(\eta^1\text{-dppm})$ complexes might be observed as well. In addition, the ability of the bridging dppm unit to maintain the two metal centers in close proximity may allow detection of hitherto elusive intermediates in the condensation reactions. With this in mind the reaction of $M(CO)_4(\eta^2\text{-alkyne})$ complexes with $M(CO)_4(\eta^1\text{-dppm})$ was investigated.

5.2. Results and Discussion

5.2.1. Reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with $M(CO)_4(\eta^1\text{-dppm})$ (M = Fe, Ru)

5.2.1.1. Synthesis and Characterization of $OsRu(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}CHCHC(O)\}(\mu\text{-dppm})$ (13) and $FeOs(CO)_6\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (18).

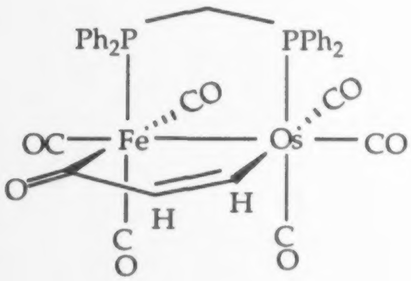
Reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ (1d) with $M(CO)_4(\eta^1\text{-dppm})$ (M = Ru, Fe) gave bimetallic complexes **13** and **18**, respectively, in good yields. The reactions required a few hours at 0°C and were completed by warming to room temperature.

The reaction between **1d** and $Ru(CO)_4(\eta^1\text{-dppm})$ gave the same product as obtained from **10a** and $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ as described in Section 4.2.1. Thus compound **13** will not be discussed further.

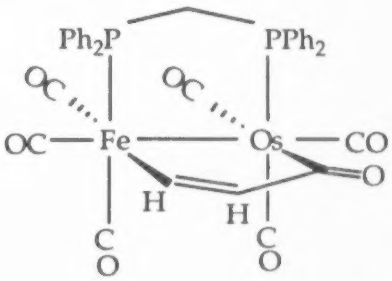
Elemental analysis and mass spectroscopy indicated that compound **18** could be formulated as $FeOs(CO)_6(C_2H_2CO)(dppm)$ (eq. 5.1).

$$\mathbf{1d} + \mathrm{Fe(CO)_4(\eta^1\text{-dppm})} \xrightarrow[0^\circ\mathrm{C} \rightarrow \mathrm{r.\,t.}]{\mathrm{CH_2Cl_2}} \underset{\mathbf{18}}{\mathrm{FeOs(CO)_6(C_2H_2CO)(dppm)}} \quad (5.1)$$

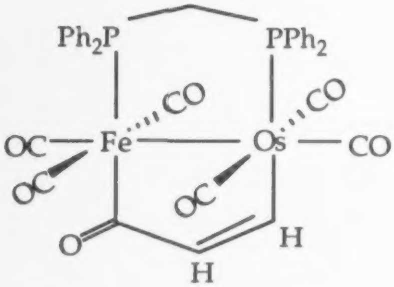
The IR, ^1H, ^{13}C NMR spectra are consistent with the formation of a dimetallacyclopentenone ring where the alkene moiety is not coordinated to a metal center.[2,4-7] Thus there are four most likely structures E', F', G', and H', where the two five-membered rings are either *cis* (E' and F') or *trans* (G' and H') to one another.


Ph2P
PPh2
CO
CO
OC
Fe
Os
CO
O
H
H
C
O
C
O

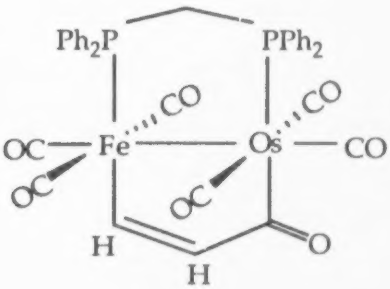
E'


Ph2P
PPh2
OC
OC
OC
Fe
Os
CO
O
H
H
C
O
C
O

F'


Ph2P
PPh2
CO
CO
OC
Fe
Os
CO
OC
OC
O
H
H

G'


Ph2P
PPh2
CO
CO
OC
Fe
Os
CO
OC
OC
H
H
O

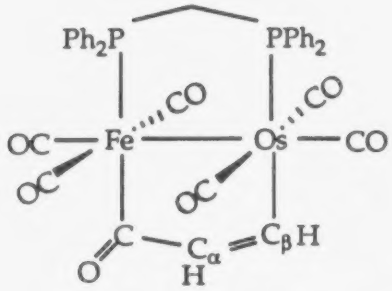
H'

In the $^{31}P\{^1H\}$ NMR spectrum of **18**, two resonances at δ 46.7 and - 14.3 were observed. The signal at δ 46.7 is assigned to the phosphorous atom of dppm that is coordinated to the iron center[8-12] while the later resonance is due to the one bonded to osmium. The ^1H NMR spectrum of compound **18** showed two signals at δ 8.47 and 3.92 in a 1:2 ratio. The resonance at δ 8.47 is typical of the β hydrogen of the $\{CH_\beta CH_\alpha C(O)\}$ group while the resonance at δ 3.92 is attributed to the methylene protons of dppm.[13-17] The presence of one methylene resonance rules out structures E' and F' as these would give rise to two chemically inequivalent protons. Selective and broad-band ^{31}P decoupling experiments clearly show that the proton signal at δ 8.47 is coupled to the osmium bonded phosphine ($^3J_{P_{Os}H}$ = 0.79 Hz) indicating that the complex has the structure G' rather than H'. Although the α proton signal of the $\{CH_\beta CH_\alpha C(O)\}$ group is hidden under the complex phenyl proton resonances (δ 7.4), it is coupled with the β proton. The coupling constant ($^3J_{HH}$ = 9.16 Hz) is characteristic of *cis* coupling in the $\{CH_\beta CH_\alpha C(O)\}$ group.[2,4,7]

The $^{13}C\{^1H\}$ NMR spectrum of **18** showed two resonances at δ 246.7 and 201.6 in a 1:6 ratio. The low field signal at δ 246.7 is assigned to the acyl group while the singlet at δ 201.6 is due to the terminal carbonyls. As the chemical shifts of iron and osmium carbonyls are typically 220 ppm and 180 ppm, respectively,[18] the appearance of the singlet at δ 201.6, which is at the average chemical shift of iron and osmium carbonyls, is rationalized in terms of a merry-go-round process, which exchanges the carbonyl ligands between Fe and Os.[19] Selective $^{13}C\{^{31}P\}$ decoupling experiments showed that the signal at δ 246.7 is coupled to the phosphine that is coordinated to the iron center, the magnitude of the coupling (18.5 Hz) indicates a *trans* relationship between the two and provides further confirmation of structure G'.[20] The additional two resonances at δ 161.3 and 139.6 are typical of the {CHCHC(O)} group.[2-7] In the ^{1}H coupled spectrum, both resonances show C-H coupling (δ 161.3, $^1J_{CH}$ = 153.4 Hz and 139.6, $^1J_{CH}$ = 148.8 Hz). The resonance at δ 139.6, which appears as a doublet of doublets of doublets, collapses to a doublet of doublets on selectively decoupling the H_β resonance at δ 8.47, showing that it belongs to the β carbon of the $\{C_\beta HC_\alpha HC(O)\}$ group (Figure 5.1). There are several examples in which the β carbon in the $\{C_\beta HC_\alpha HC(O)\}$ group is located at higher field than the α carbon.[4] Consistent with this assignments, selective $^{13}C\{^{31}P\}$ decoupling experiments clearly showed that the resonance at δ 139.6 is strongly coupled to the Os-bound phosphorus atom (41.3 Hz), indicating that they are *trans* to each other. Thus the NMR data unequivocally establish that compound **18** has structure G'.

5.2.1.2. Reaction of 13 with CO: Synthesis and Characterization of $OsRu(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_2C(O)\}(dppm)$ (15). Stirring a dichloromethane solution of compound **13** under carbon monoxide atmosphere for 5 h resulted in the formation of the new compound **15** (e.q. 5.2). In the IR spectrum the acyl band of **13** at 1707 cm^{-1} has shifted to 1605 cm^{-1}, a region characteristic of the acyl group of dimetallacyclopentenone, where the alkene moiety is not coordinated to a metal center.[2,4,7]

$$\mathbf{13} \quad + \quad CO \xrightarrow[CH_2Cl_2]{} \underset{\mathbf{15}}{OsRu(CO)_5(C_2H_2CO)(dppm)} \qquad (5.2)$$


Ph2P
PPh2
CO
CO
OC
Fe
Os
CO
OC
OC
O
C
Cα
H
CβH

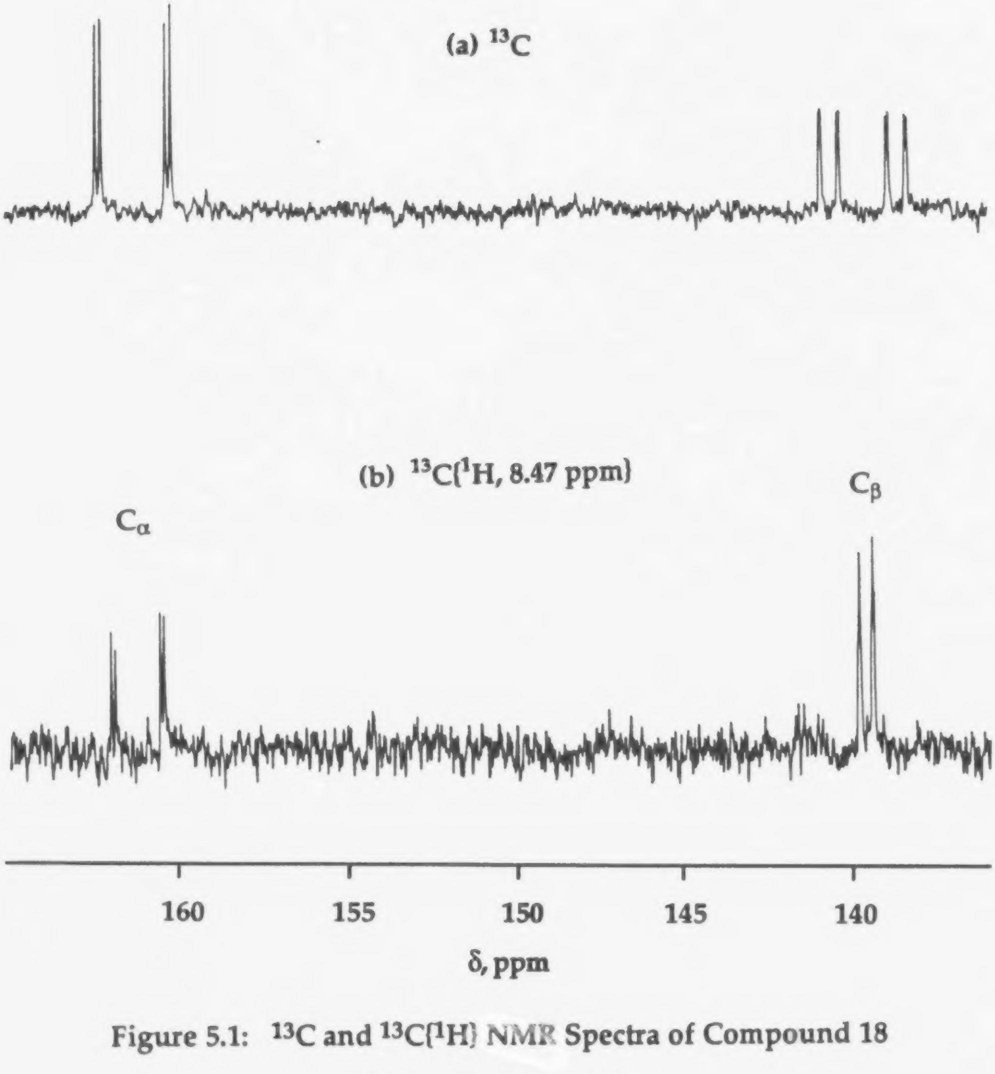
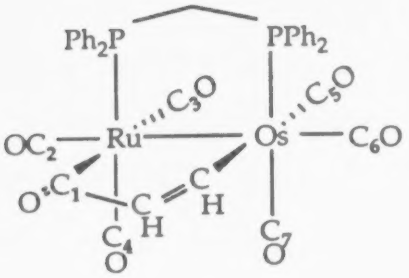


Figure 5.1: ^{13}C and $^{13}C\{^1H\}$ NMR Spectra of Compound 18

in the Olefin Region

In the $^{31}P\{^1H\}$ NMR spectrum, two doublets were observed at δ 20.9 and - 16.7 due to the Ru and Os-bound phosphorus atoms, respectively. The ^1H NMR spectrum showed two low-field signals at δ 8.18 and 7.72 in the typical range of the β and α hydrogens of the $\{CH_\beta CH_\alpha C(O)\}$ group.[2,4,7] Selective ^{31}P decoupling experiments indicated that both hydrogens are only coupled to the Os-bound phosphine. The $^{13}C\{^1H\}$ NMR spectrum (Figure 5.2), showed a low-field signal at δ 250.7, due to the acyl group, and six terminal carbonyl resonances at δ 201.6, 199.6, 188.8, 185.9, 183.6, and 172.0. This sample of **15** was obtained by reacting **13**, approximately 50% enriched in ^{13}CO, with ^{13}CO.

Selective and broad-band ^{31}P decoupling experiments clearly differentiated the Ru-bound carbonyls from those on Os. Upon selectively decoupling the ^{31}P resonance at δ 20.9 (belonging to Ru), the ^{13}C O resonances at δ 250.7 ($^2J_{CP_{Ru}}$ = 11.1 Hz), 201.6 ($^2J_{CP_{Ru}}$ = 89.5 Hz), 199.6 ($^2J_{CP_{Ru}}$ = 10.2 Hz), and 188.8 ($^2J_{CP_{Ru}}$ = 13.1 Hz) simplified accordingly, while they remained unchanged when the other ^{31}P resonance was decoupled, indicating that they are bound to ruthenium. The large coupling between the carbonyl at δ 201.6 and the phosphine suggests that they are *trans* to each other. A broad-band ^{31}P decoupling experiment showed that the carbonyl at δ 199.6 is strongly coupled to the acyl group at δ 250.7 (20 Hz), indicating that they are located *trans* to one another. The three doublets at δ 185.9 ($^2J_{CP_{Os}}$ = 92.6 Hz), 183.6 ($^2J_{CP_{Os}}$ = 8.0 Hz), and 172.0 ($^2J_{CP_{Os}}$ = 9.1 Hz) collapsed to three singlets upon selectively decoupling the phosphorus resonance at δ - 16.7. This demonstrates that these three carbonyls are bound to the osmium center. The large coupling between the carbonyl at δ 185.9 and the phosphine (92.6 Hz) indicates that they are located in *trans*


Ph₂P
PPh₂
C₃O
C₅O
OC₂
Ru
Os
C₆O
O
C₁
C
H
C
H
C₄
O
C₇
O

15

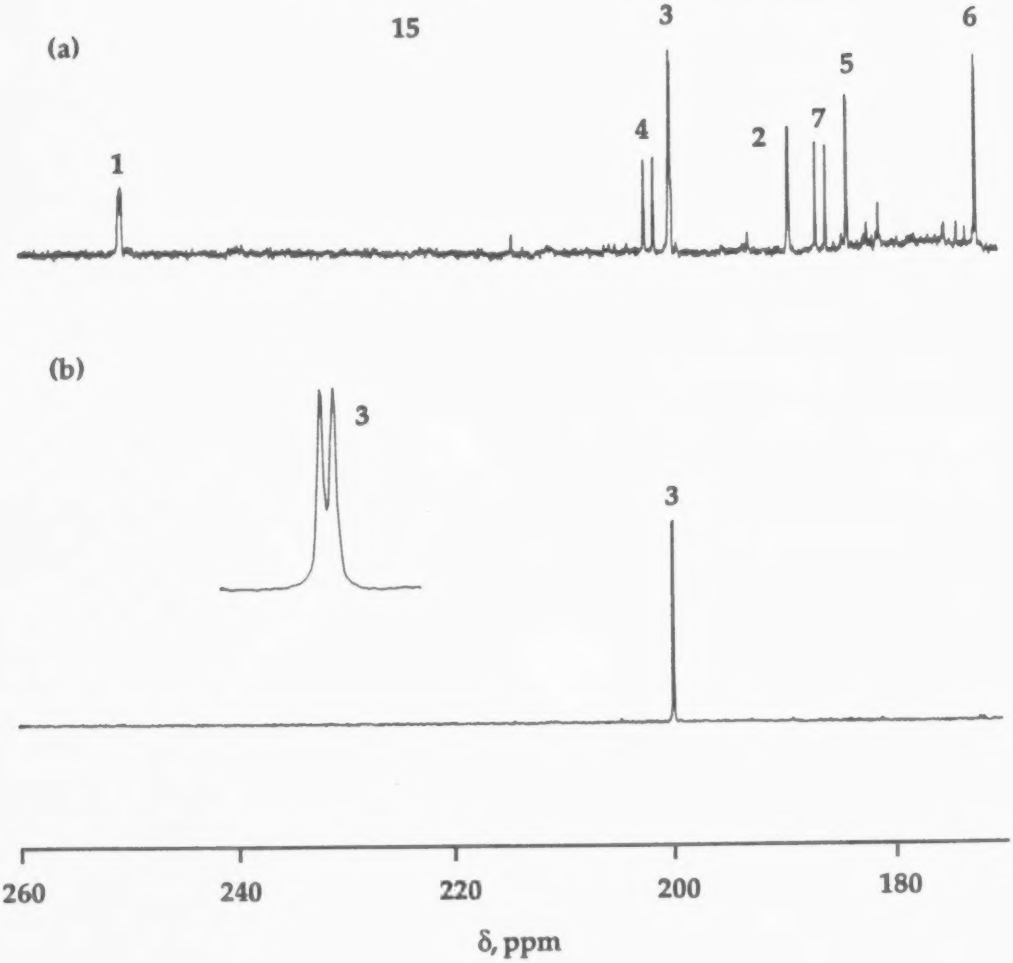
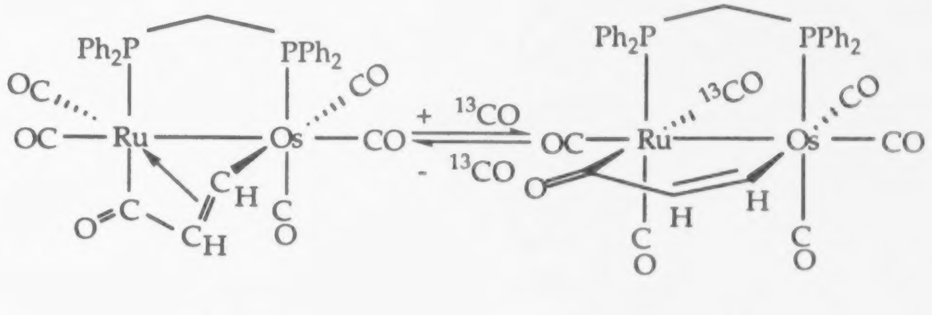


Figure 5.2: $^{31}C\{^{1}H\}$ NMR Spectra of Compound 15: (a) from the reaction of compound 13 (50 % ^{13}CO enriched) with ^{13}CO; (b) from the reaction of compound 13 (without carbonyl enrichment) with ^{13}CO

positions. Furthermore, an interesting observation is that the intensity of the carbonyl at δ 199.6 is about twice that of the other carbonyls, suggesting that the ^{13}CO has been introduced specifically to one site of the ruthenium center in the reaction of compound **13** with ^{13}CO. This will be discussed fully in the next section. Thus, the NMR data are consistent with the structure shown in Figure 5.2.

5.2.1.3. Interconversion between Compound 13 and Compound 15. In the previous section, the reaction of compound **13** with carbon monoxide to give compound **15** was described. Subsequently, an attempt to investigate the reverse reaction was carried out by purging a dichloromethane solution of compound **15** with nitrogen. After 30 min., compound **15** was quantitatively decarbonylated to afford compound **13**, identified by IR and NMR spectroscopy (e.q. 5.3). Because of the rapid decarbonylation at ambient temperature, the NMR spectra of compound **15** had to be obtained at low temperatures or under a CO atmosphere.



(5.3)

13 **15**

As mentioned earlier, the ^{13}C{^{1}H} NMR spectrum of **15**, prepared from about 50% ^{13}CO enriched **13** and ^{13}CO, showed that the intensity of the carbonyl signal at δ 199.6 was twice that of other carbonyls, hinting that the addition of ^{13}CO occured *trans* to the acyl group. Confirmation came from conversion of **15** to **13** by purging the solution with N_2. It was found that the acyl group and the carbonyl signals in the resulting **13** have the same intensity, indicating that it is the carbonyl that was introduced from ^{13}CO that had dissociated from species **15**.

Further experiments were carried out to verify the site specificity of interconversion (e.q. 5.3). The reaction of $RuOs(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_2H_2C(O)\}(\mu\text{-}dppm)$ (**13**) (natural abundance ^{13}CO) with ^{13}CO led to incorporation of ^{13}CO exclusively into the site *trans* to the acyl moiety (Figure 5.2). In the corresponding $^{31}P\{^1H\}$ NMR spectrum, the Ru-bound ^{31}P resonance at δ 20.9 showed an additional doublet splitting due to $^2J_{CP_{Ru}} = 10.2$ Hz, while the other phosphorus resonance at δ - 16.7 remained a simple doublet ($^2J_{PP} = 68.2$ Hz). When this solution was purged with N_2 at room temperature, decarbonylation and formation of **13** was complete in 30 min. The $^{31}P\{^1H\}$ NMR spectrum of **13** showed two doublets at δ 30.8 and 8.4 ($^2J_{PP} = 120$ Hz). The absence of additional coupling to carbonyl (^{13}CO) also suggests that it is the ^{13}CO ligand in species **15** that had been completely dissociated. Consistent with this observation, in the $^{13}C\{^1H\}$ spectrum no carbonyl signals were observed after the same number of scans were collected as in the previous $^{13}C\{^1H\}$ experiment on **15**. Clearly, the interconversion between species **13** and **15** is site specific. It is interesting to note that the analogous $OsRu(CO)_8\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_2C(O)\}$ compound is stable at room temperature and does not undergo CO elimination.[2] This indicates that the cis-labilization of the phosphine ligand is important in facilitating cis-CO dissociation.[21-24] The reason for the specificity is likely the trans effect of the strong σ-bonding acyl group which labilizes the carbonyl ligand *trans* to it.[20,25-30] The 16-electron species is then stabilized by coordination of the double bond of dimetallacyclopentenone. By the principle of microscopic reversibility, it is expected that CO addition to **13** will end up *trans* to the acyl group. Since the carbonyl ligands do not scramble in either **13** or **15**, the integrity of the initial attack is maintained.

5.2.1.4. Formation of Compound 13. In order to obtain information about the mechanism of formation of compound **13**, the reaction of $Ru(CO)_4(\eta^1\text{-dppm})$ with $Os(CO)_4(\eta^2\text{-}C_2H_2)$ was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy at different temperatures (Figure 5.3). From - 80°C to - 20°C, no new species were observed aside from the starting materials. At - 10°C, the $^{31}P\{^1H\}$ NMR spectrum showed two new species **16** and **17**, each with two ^{31}P doublets. For compound **16**, the doublet at δ 31.2 ($^2J_{PP}$ = 25.4 Hz) is assigned to the Ru-bound phosphorus atom while the doublet at δ - 9.2 ($^2J_{PP}$ = 25.4 Hz) to that bound to osmium. The relatively small coupling between the phosphorus nuclei (25.4 Hz) suggests that there is no ruthenium-osmium bond present in this intermediate (Scheme 5.1). This suggestion is based on similar observations reported by Shaw[9] who showed that the $^2J_{PP}$ coupling constants in μ-dppm complexes in which there is no metal-metal bond, such as $(OC)_4Fe(\mu\text{-dppm})Mo(CO)_5$ ($^2J_{PP}$ = 27 Hz) and $(OC)_4Fe(\mu\text{-dppm})Mn(CO)_4Br$ ($^2J_{PP}$ = 37 Hz), are much smaller than in the corresponding compounds where a dative metal-metal bond is present, $(OC)_4Fe(\mu\text{-dppm})Mo(CO)_4$ ($^2J_{PP}$ = 85 Hz) and $(OC)_4Fe(\mu\text{-dppm})Mn(CO)_3Br$ ($^2J_{PP}$ = 78 Hz). The ^1H NMR spectrum of **16** shows a doublet at δ 6.03 ($^3J_{HP}$ = 2.0 Hz) and a doublet of doublets at δ 3.47 ($^2J_{CP_{Ru}} = {}^2J_{CP_{Os}}$ = 7.5 Hz), integrating as two protons each. The chemical shift at δ 6.03 is very similar to that of $Os(CO)_4(\eta^2\text{-}C_2H_2)$[2] while the other resonance at δ 3.47 is characteristic of the methylene protons of dppm.[13-17,31] The $^{13}C\{^1H\}$ NMR spectrum of **16**, obtained from monitoring the reaction of $Ru(^{13}CO)_4(\eta^1\text{-dppm})$ with $Os(^{13}CO)_4(\eta^2\text{-}C_2H_2)$, showed two carbonyl resonances in the region typical of Os-bound carbonyls at δ 175.3 ($^2J_{CP_{Os}}$ = 117 Hz) and 186.1 ($^2J_{CP_{Os}}$ = 10.1 Hz) with an intensity ratio of 1:2. The corresponding $^{31}P\{^1H\}$ NMR spectrum clearly showed that these doublets were due to coupling to the Os-bound phosphorus nucleus. The large splitting (117 Hz) of the carbonyl signal at δ 175.3 indicates a carbonyl *trans* to the Os-bound phosphorus nucleus,[20] while the other carbonyls at δ 186.1 are *cis* to the phosphorus atom. There is an additional resonance at δ 204.1 belonging to **16**, the signal overlaps with that due to unreacted $Ru(^{13}CO)_4(\eta^1\text{-dppm})$ starting material, suggesting that they have similar structures. As found in the related compounds $Ru(CO)_4L$ (L = dppm, PR_3),[13,32] the presence of only one resonance for the Ru-bound carbonyls, even down to - 110°C, implies that the carbonyls bound to Ru are fluxional. Rapid axial-equatorial carbonyl exchange process can be rationalized in terms of the well-known Berry pseudorotation mechanism.[33] For species **17**, the two ^{31}P doublets at δ 21.5 and - 16.7 are assigned to the Ru- and Os-bound phosphorus. More importantly, the coupling constant (76.3 Hz) between the phosphorus nuclei is significantly larger than that found in species **16** and indicates the formation of a metal-metal bond. In the ^1H NMR spectrum, two signals at δ 8.59 and 7.75, belonging to **17**, are characteristic of the β and α protons of a $\{CH_{\beta}CH_{\alpha}C(O)\}$ group where the alkene moiety is not coordinated to a metal center.[2,7] Two resonances at δ 4.63 and 3.88 are typical of the methylene protons of dppm. Based on these data the structure of **17** is proposed as shown in Scheme 5.1. The presence of donor-acceptor $Ru \rightarrow Os$ bond is to satisfy the 18-electron rule, but it may also help promoting the CO insertion reaction. The possibility

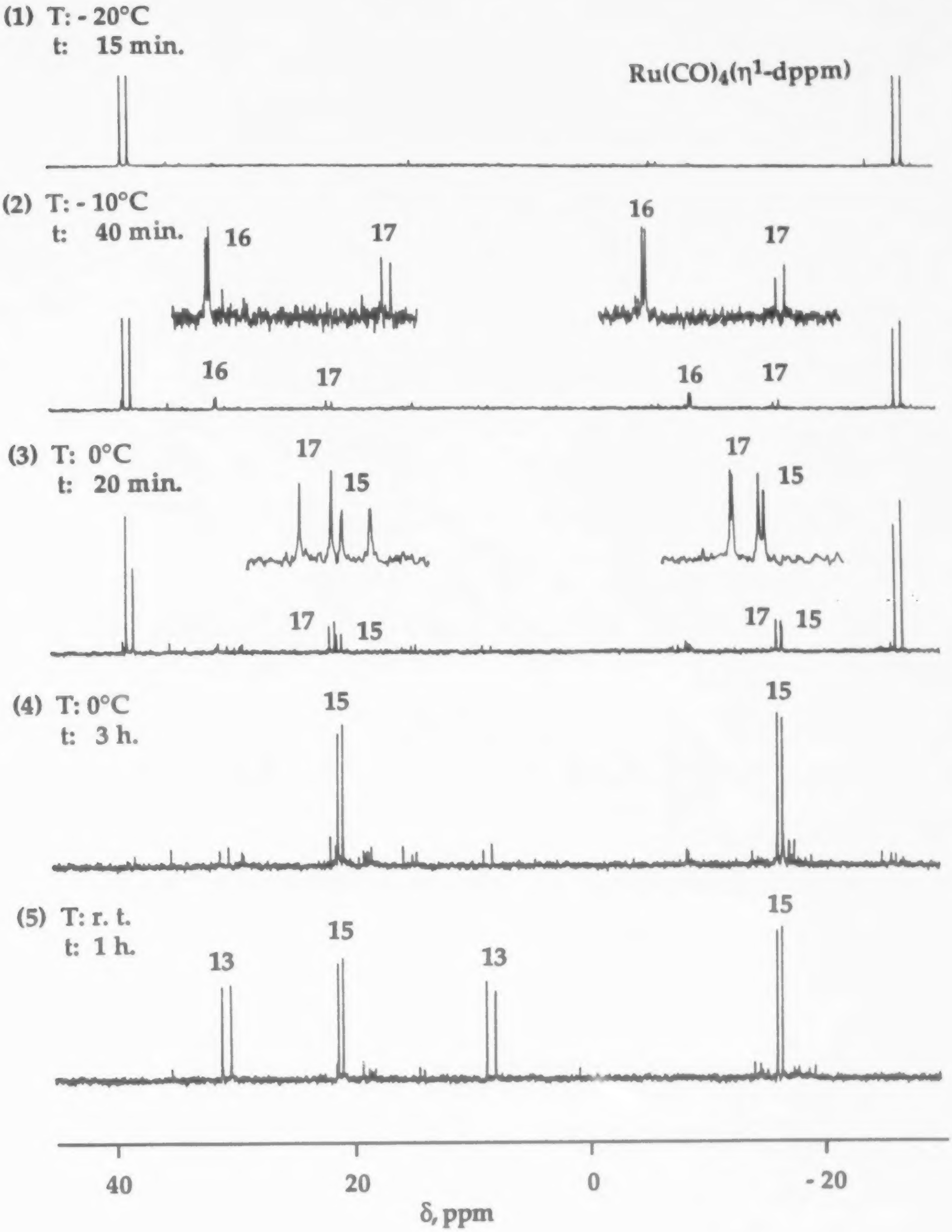
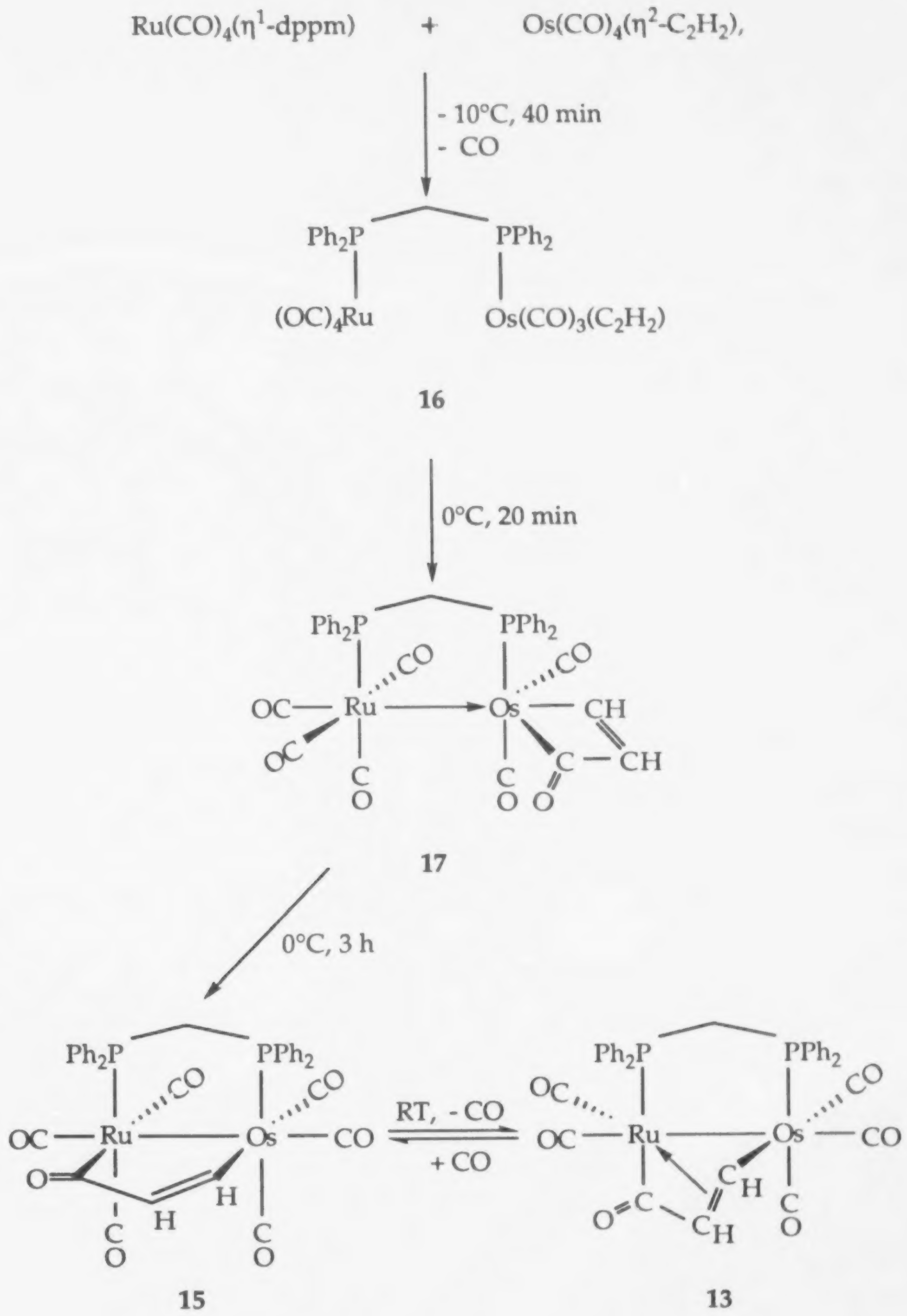


Figure 5.3: $^{31}P\{^1H\}$ NMR Monitoring of the Reaction of $Ru(CO)_4(\eta^1\text{-dppm})$ with $Os(CO)_4(\eta^2\text{-}C_2H_2)$: Formation of 13


Ru(CO)$_4$(η^1-dppm) + Os(CO)$_4$(η^2-C$_2$H$_2$),
- 10°C, 40 min
- CO
Ph$_2$P
PPh$_2$
(OC)$_4$Ru
Os(CO)$_3$(C$_2$H$_2$)
16
0°C, 20 min
17
0°C, 3 h
RT, - CO
+ CO
15
13

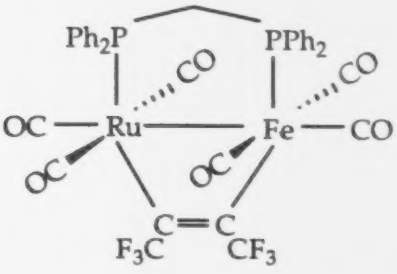
Scheme 5.1: Mechanism for the Formation of 13 that, instead of Ru→Os bond, a side-on bonded Ru-CO fulfills the electronic demand of the Os center can not be ruled out. Unfortunately the complicated nature of the ^{13}C NMR spectrum and the small concentration of **17** at this stage of the reaction prevented its clear identification. Warming to 0°C results in conversion of **17** to **15**. This is an interesting and crucial observation since it shows that ring expansion of metallacyclobutenone to dimetallacyclopentenone is a definite possibility along the condensation reaction pathway. As already mentioned in Chapter 4, on warming to room temperature, species **15** converts to the final product **13**.

5.2.2. Reaction of $Ru(CO)_4(\eta^2\text{-}CF_3C_2CF_3)$ with $Fe(CO)_4(\eta^1\text{-dppm})$

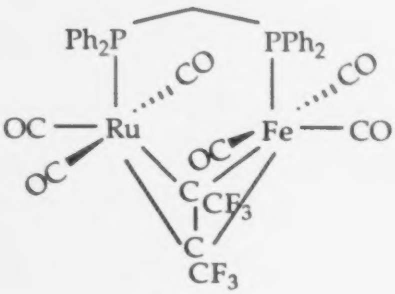
As mentioned in the introduction, the products of condensation reactions of $M(CO)_4(\eta^2\text{-alkyne})$ with other 18-electron species depend on the metal and the alkyne. In contrast to the reaction of $Fe(CO)_4(\eta^1\text{-dppm})$ with $Os(CO)_4(\eta^2\text{-}C_2H_2)$, which gave dimetallacyclopentenone **15** and **13**, its reaction with $Ru(CO)_4(\eta^2\text{-}CF_3C_2CF_3)$ gave a dimetallacyclobutene species, $FeRu(CO)_6(\mu\text{-}CF_3C_2CF_3)(\mu\text{-dppm})$ (**20**) (eq. 5.4).

$$\mathbf{1c} \xrightarrow[CH_2Cl_2/\text{pentane, 43 h}]{+\ Fe(CO)_4(\eta^1\text{-dppm})} \underset{\mathbf{20}}{FeRu(CO)_6(\mu\text{-}CF_3C_2CF_3)(\mu\text{-dppm})} \quad (5.4)$$

Formulation of **20** is based on elemental analysis and spectroscopic data. The ^1H NMR spectrum displayed a triplet at δ 3.58 corresponding to the methylene protons of dppm, implying that these two protons are equivalent. Thus there are two possible structures, I' with a two-electron alkyne and a Fe-Ru bond and J' with a four-electron alkyne and no Fe-Ru bond.



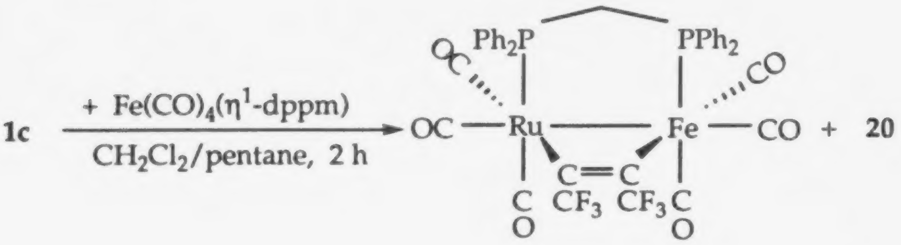
I'



J'

In the ^{19}F NMR spectrum two resonances at δ - 55.5 and - 56.9 were observed, which is consistent with structure **I'** instead of **J'** as the latter would render the two sets of CF_3 groups equivalent. The $^{31}P\{^1H\}$ NMR spectrum showed two signals at δ 63.7 and 33.5 for the phosphorus atoms bound to Fe and Ru, respectively.[12,13] Both the down-field shifts with respect to that of free dppm (δ 22.7) and the strong coupling (100.4 Hz) between the phosphorus nuclei suggest the formation of a five-membered ring[34,35] and a metal-metal bond.[9] The room temperature $^{13}C\{^1H\}$ NMR spectrum exhibited only one resonance in the terminal carbonyl region at δ 208.1. As the chemical shifts of the terminal carbonyls bound to Fe and Ru are around 220 ppm and 200 ppm, respectively,[18] the presence of one singlet at the approximately average position is indicative of rapid carbonyl scrambling. The carbonyl exchange process is best accounted by the well-known "merry-go-round" carbonyl exchange process,[19] and has been observed in the related $Ru_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^1\text{-HFB})$.[1] Thus, the NMR data are clearly consistent with structure I' for species **20**.

When the reaction of $Fe(CO)_4(\eta^1\text{-dppm})$ with $Ru(CO)_4(\eta^2\text{-HFB})$ was carried out for only 2 h, a mixture of compounds **19** and **20**, in a ratio of 1:1.3 was obtained (eq. 5.5).



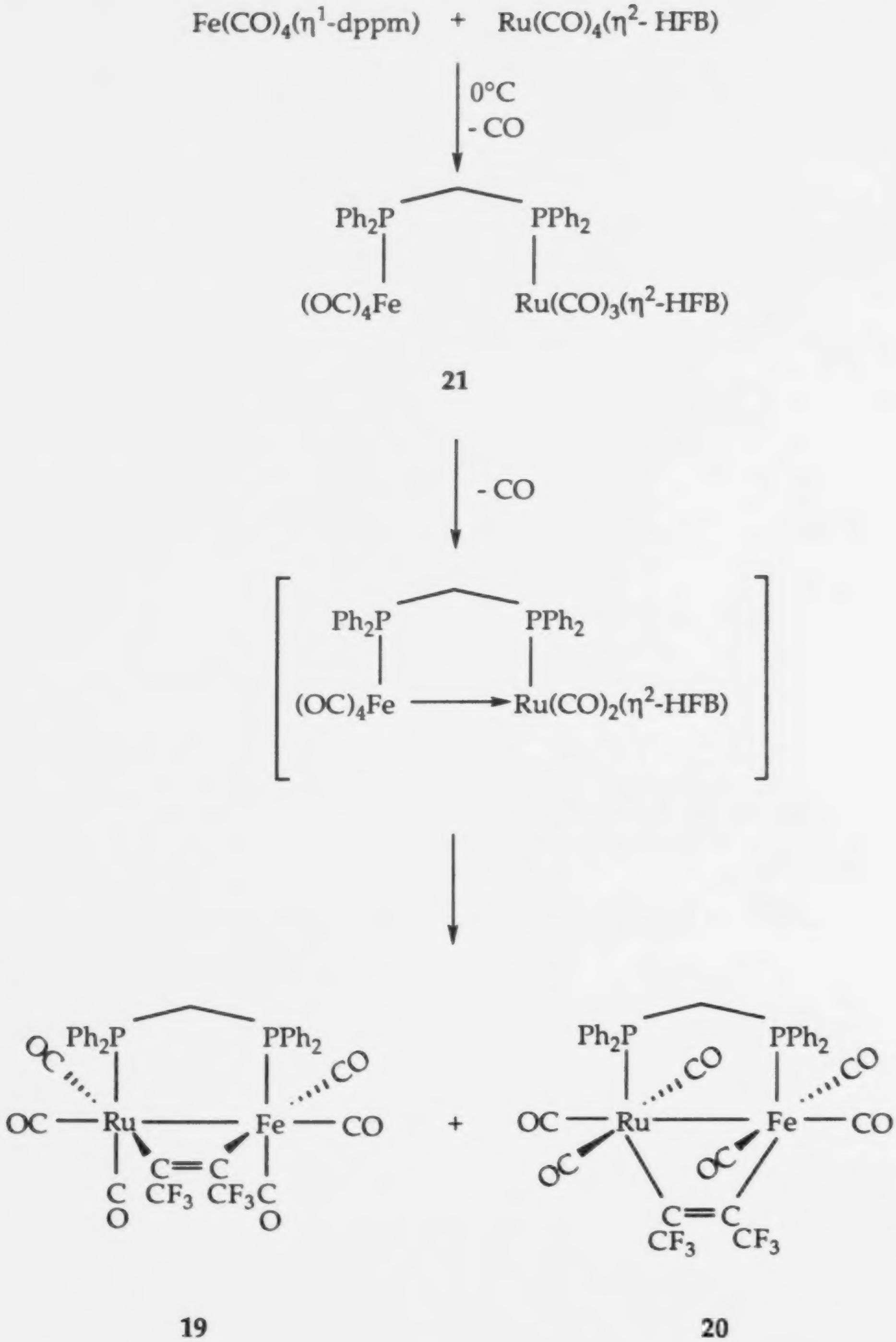
(5.5)

19

Formulation of **19** is based on NMR spectroscopic data. The ^1H NMR spectrum displayed two resonances, belonging to **19**, at δ 4.18 and 3.33, which are due to the methylene protons of dppm. The $^{31}P\{^1H\}$ NMR spectrum showed two doublets at δ 43.3 and 20.0 that belong to **19**. Again, the down-field shifts of the coordinated dppm resonances with respect to that of free dppm implies that a five-membered ring has formed. Consistent with this, the relatively large coupling (55.2 Hz) between the phosphorus nuclei also supports the formation of a metal-metal bond. Furthermore, the observation of two signals at δ - 53.3 and - 55.5 in the ^{19}F NMR spectrum, indicating inequivalent CF_3 groups, is in accord with the structure as illustrated in eq. 5.5.

In an attempt to obtain information about the mechanism of formation of compounds **19** and **20**, the reaction of $Ru(CO)_4(\eta^2\text{-HFB})$ with $Fe(CO)_4(\eta^1\text{-dppm})$ was monitored by $^{31}P\{^1H\}$ and ^{19}F NMR spectroscopy at low temperatures (Scheme 5.2). At 0°C, the $^{31}P\{^1H\}$ NMR spectrum showed a new species **21**, with signals at δ 66.4 and 25.7 due to the Fe- and Ru-bound phosphorus atoms, respectively. The small coupling (36.2 Hz) between the phosphorus nuclei indicates that there is no metal-metal bond present. The ^{19}F NMR spectrum displayed a doublet at δ - 54.4 ($^4J_{PF}$ = 1.5 Hz), which is consistent with the equivalence of the two sets of CF_3 groups. When the temperature was raised to room temperature, no other intermediates were seen but both species **19** and **20** started to appear in the $^{31}P\{^1H\}$ and ^{19}F spectra. When the solution was maintained at room temperature, compound **19** gradually converted to compound **20**.

Consistent with the facile CO substitution of $Ru(CO)_4(\eta^2\text{-HFB})$ with monophosphines described in Chapter 2, the reaction proceeds by initial CO loss from $Ru(CO)_4(\eta^2\text{-HFB})$ followed by attachment of the dangling phosphine of $Fe(CO)_4(\eta^1\text{-dppm})$ to afford intermediate **21**. Since both metals in compound **21** are coordinatively saturated, the following step of the reaction could proceed by CO dissociation from either the ruthenium center or the iron center. Dissociation of CO from $Ru(CO)_3(PR_3)(\eta^2\text{-HFB})$ complexes takes place readily at room temperature, while CO dissociation from $Fe(CO)_4(\eta^1\text{-dppm})$ does not occur even at 80°C.[12] This suggests that the CO dissociation in species **21** is most likely to take place at the ruthenium center to give $(OC)_4Fe(\mu\text{-dppm})Ru(CO)_2(\eta^2\text{-HFB})$ where a $Fe \rightarrow Ru$ dative bond is proposed to maintain the 18-electron configuration at the ruthenium center. Such a dative bond is typical of dinuclear complexes containing $Fe(CO)_4(dppm)$ unit such as $(OC)_4Fe(\mu\text{-dppm})Mn(CO)_4Br$ in which a $Fe \rightarrow Mn$ dative bond was proposed.[9,12,36] This species then converts to products **19** and **20**. Since **19** slowly isomerizes to compound **20**, this implies that it is the kinetic product and compound **20** is thermodynamically more stable. The slow isomerization process could involve switching of the two electron HFB to a


Fe(CO)4(η1-dppm) + Ru(CO)4(η2- HFB)
0°C
- CO
Ph2P
PPh2
(OC)4Fe
Ru(CO)3(η2-HFB)
21
- CO
Ph2P
PPh2
(OC)4Fe
Ru(CO)2(η2-HFB)
Ph2P
PPh2
OC
Ru
Fe
CO
C=C
CF3
CF3C
O
+
19
20

Scheme 5.2: Mechanism for the Formation of 19 and 20 four electron mode with concomitant cleavage of the Fe-Ru bond, i.e. structure J'. Similar bonding mode changes of alkyne ligands have been observed in several dinuclear complexes.[1,37-41]

5.3. Conclusions

The results of this study show that $M(CO)_4(\eta^2\text{-alkyne})$ (M = Os, alkyne = C_2H_2; M= Ru, alkyne = $CF_3C_2CF_3$) compounds react readily with $M'(CO)_4(\eta^1\text{-dppm})$ (M' = Fe, Ru) to yield two types of dimetallacyclic complexes.

The reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with $M'(CO)_4(\eta^1\text{-dppm})$ (M' = Fe, Ru) gives the corresponding dimetallacyclopentenone compounds **13** and **18**. For the reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with $Fe(CO)_4(\eta^1\text{-dppm})$, mechanistic studies showed that the reaction proceeds by initial CO substitution in $Os(CO)_4(\eta^2\text{-}C_2H_2)$ by the free phosphine end of $Fe(CO)_4(\eta^1\text{-dppm})$ to yield species **16**. This species then undergoes CO insertion at the osmium center to generate an osmacyclobutenone species **17** that is stabilized by a ruthenium to osmium dative bond. These steps are analogous to those identified in the reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with dppm. The following step involves ring expansion of osmacyclobutenone from intermediate **17** to generate dimetallacyclopentenone **15**. It is interesting that this species undergoes facile CO dissociation to yield the final product **13**. While the conversion of compound **15** to compound **13** is reversible, it is clear that the CO ligand dissociates from a position *trans* to the acyl group at the ruthenium center; this is attributed to a combination of cis-labilization of the phosphine ligand, the strong trans effect of the acyl group and the weak Ru-CO bond energy.[42] In contrast, $FeOs(CO)_6\{\mu$-

$C_2H_2C(O)\}(\mu$-dppm) (**18**) resists CO dissociation from the iron center. Undoubtedly this is a consequence of both the different geometry of the complex and the stronger bond between iron and carbon monoxide compared to that between ruthenium and CO.[42]

The reaction of $Ru(CO)_4(\eta^2$-HFB) with $Fe(CO)_4(\eta^1$-dppm) affords the dimetallacyclobutene compounds **19** and **20**. The reaction proceeds via intermediate **21** which is formed in a similar fashion to **16** described above. This species then undergoes further CO dissociation from the ruthenium center, followed by alkyne migration from a terminal to a bridging position to yield compounds **19** and **20**. Isomerization of **19** to **20** may involve bonding mode change of the alkyne from parallel, two electron donor ligand, to perpendicular four electron donor ligand and reformation of the dimetallacyclobutene core of **20**.

These studies provide further examples that the reaction of $M(CO)_4(\eta^2$-alkyne) (M = Os, alkyne = C_2H_2; M= Ru, alkyne = $CF_3C_2CF_3$) with $M'(CO)_4(\eta^1$-dppm) (M' = Fe, Ru) is both metal and alkyne dependent. The formation of two types of products, dimetallacyclopentenone and dimetallacyclobutene, are analogous to those from the condensation reactions of $M(CO)_4(\eta^2$-alkyne) (M = Os, alkyne = C_2H_2; M= Ru, alkyne = $CF_3C_2CF_3$) with other 18-electron compounds such as $Ru(CO)_5$. This indicates that, in general, the intermediates observed here should be closely related to those in the condensation reactions of $M(CO)_4(\eta^2$-alkyne) with other 18-electron compounds.

5.4. Experimental Section

5.4.1. Starting Materials and Reagents

$Fe_2(CO)_9$ was purchased from Alfa Chemical Company. The compounds $Fe(CO)_4(\eta^1\text{-dppm})$[9] and $Ru(CO)_4(\eta^1\text{-dppm})$[13] were prepared by the published procedures.

5.4.2. Synthetic Procedures

Synthesis of $OsRu(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^3\text{-CHCHC(O)}\}(\mu\text{-dppm})$, 13

A solution of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ (50 mg, 0.152 mmol) in pentane (25 mL) was added to a reddish brown solution of $Ru(CO)_4(\eta^1\text{-dppm})$ (91 mg, 0.152 mmol) in CH_2Cl_2 (10 mL) at - 5°C. The reaction mixture was then placed in an ice/water bath and kept stirring under a stream of argon at 0°C for 2 h. Over this time the orange solution gradually changed to an orange suspension. The mixture was then allowed to warm to ambient temperature and was stirred for 5 h. The solvent was removed in vacuo. Recrystallization from CH_2Cl_2/pentane gave **13** as a yellow solid 107 mg (81%). The spectroscopic data are listed in Section 4.4.2.

Synthesis of $RuOs(CO)_6\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$, 15

A dichloromethane solution of compound **13** was stirred under carbon monoxide atmosphere at room temperature for 5 h. Over this time no obvious color change took place. The reaction was monitored by IR spectroscopy and showed quantitative formation of compound **15**.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2071 s, 2035 s, 2002 s, 1989 sh, 1960 m; υ_{acyl}: 1605 w.

^{1}H NMR (0°C): 8.19 (dd, $^3J_{HH}$ = 9.60 Hz, $^3J_{P_{Os}H}$ = 2.04 Hz, 1H), 7.72 (dd, $^3J_{HH}$ = 9.60 Hz, $^4J_{P_{Os}H}$ = 4.08 Hz, 1H), 4.90 (dt, $^2J_{HH}$ = 14.20 Hz, $^2J_{P_{Os}H}$ = 10.83 Hz, $^2J_{P_{Ru}H}$ = 10.92 Hz, 1H), 4.43 (m, $^2J_{HH}$ = 14.20 Hz, $^2J_{P_{Os}H}$ = 13.39 Hz, $^2J_{P_{Ru}H}$ = 11.40 Hz, 1H).

^{31}P{^{1}H} NMR (0°C): 20.9 (d, $^2J_{PP}$ = 68.2 Hz, P-Ru), - 16.7 (d, $^2J_{PP}$ = 68.2 Hz, P-Os).

^{13}C{^{1}H} NMR (- 40°C): 250.7 (dd, $^2J_{acyl\text{-}CO}$ = 21.0 Hz, $^2J_{P_{Ru}C}$ = 11.1 Hz, acyl), 201.6 (d, $^2J_{P_{Ru}C}$ = 89.5 Hz, 1CO), 199.6 (m, $^2J_{acyl\text{-}CO}$ = 21.0 Hz, $^2J_{P_{Ru}\text{-}C}$ = 10.2 Hz, 1CO), 188.8 (d, $^2J_{P_{Ru}C}$ = 13.1 Hz, 1CO), 185.9 (d, $^2J_{P_{Os}C}$ = 92.6 Hz, 1CO), 183.6 (d, $^2J_{P_{Os}C}$ = 8.0 Hz, 1CO), 172.0 (d, $^2J_{P_{Os}C}$ = 9.1 Hz, 1CO).

Characterization of RuOs(CO)$_7$(η^2-C$_2$H$_2$)(μ-dppm), 16

^{1}H NMR(- 10°C): 6.03 (d, $^3J_{PH}$ = 2.0 Hz, C$_2$H$_2$), 3.47 (dd, $^2J_{PH}$ = 7.5 Hz, 2H).

^{31}P{^{1}H} NMR(- 10°C): 31.2 (d, $^2J_{PP}$ = 25.4 Hz, P-Ru), - 9.2 (d, $^2J_{PP}$ = 25.4 Hz, P-Os).

^{13}C{^{1}H} NMR (- 10°C): 204.1 (Ru-CO), 186.1 (d, $^2J_{P_{Os}C}$ = 10.1 Hz, 2CO), 175.3 (d, $^2J_{P_{Os}C}$ = 117 Hz, 1CO).

Characterization of RuOs(CO)$_6${η^2-C$_2$H$_2$C(O)}(μ-dppm), 17

^{1}H NMR (0°C): 8.59 (d, $^3J_{HH}$ = 9.4 Hz, 1H), 7.75 (dd, $^3J_{HH}$ = 9.4 Hz, $^4J_{PH}$ = 8.8 Hz, 1H), 4.63 (m, 1H), 3.88 (m, 1H).

^{31}P{^{1}H} NMR (0°C): 21.5 (d, $^2J_{PP}$ = 76.3 Hz, P-Ru), - 16.7 (d, $^2J_{PP}$ = 76.3 Hz, P-Os).

Synthesis of FeOs(CO)$_6${μ–η^1:η^1--C$_2$H$_2$C(O)}(μ-dppm), 18

A colorless solution of Os(CO)$_4$(η^2-C$_2$H$_2$) (50 mg, 0.153 mmol) in pentane (12 mL) was added to a reddish brown solution of

$Fe(CO)_4(\eta^1$-dppm) (84 mg, 0.153 mmol) in CH_2Cl_2 (7 mL) at 0°C, which resulted in the formation of an orange suspension. The reaction mixture was stirred under a stream of argon at 0°C for 3 h. The suspension gradually turned to an orange solution and then changed back to an orange suspension. The ice bath was removed and the mixture was allowed to warm to room temperature and kept stirring at room temperature for additional 2 h. The solvent was then removed in vacuo. The residue was recrystallized from CH_2Cl_2/pentane to give **18** as a yellow powder (101 mg, 78%). Anal. Calcd. for $C_{34}H_{24}O_7P_2FeOs$: Calcd: C, 47.90; H, 2.84. Found: C, 48.24: H, 2.91. MS (FAB): M^+= - nCO, n = 0-6.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2079 w, 2014 s, 2002 vs, 1964 m, 1934 m; υ_{acyl}: 1604 w.

^1H NMR: 8.47 (dd, $^3J_{POsH}$ = 0.79 Hz, $^3J_{HH}$ = 9.16 Hz, 1H), 3.92 (dd, $^2J_{POsH}$ = 10.64 Hz, $^2J_{PFeH}$ = 9.56 Hz, 2H).

$^{31}P\{^1H\}$ NMR: 46.7 (d, $^2J_{PP}$ = 83.7 Hz, P-Fe), - 14.3 (d $^2J_{PP}$ = 83.7 Hz, P-Os).

$^{13}C\{^1H\}$ NMR: 246.7 (dd, $^2J_{PFeC}$ = 18.5 Hz, $^3J_{POsC}$= 9.7 Hz, acyl), 201.6 (s, 6CO), 161.3 (d, $^3J_{PFeC}$ = 11.7 Hz, Fe-C(O)-C(H)-), 139.6 (dd, $^2J_{POsC}$ = 41. 3 Hz, $^3J_{PFeC}$ = 3.3 Hz, Os-C(H)=), 48.3 (dd, $^1J_{POsC}$ = 28.4 Hz, $^1J_{PRuC}$ = 19.3 Hz, $PPh_2CH_2PPh_2$)

Synthesis of $FeRu(CO)_6\{\mu$-η^1:η^1-$C_2(CF_3)_2\}(\mu$-dppm), 20

A colorless solution of $Ru(CO)_4(\eta^2$-HFB) (50mg, 0.133 mmol) in 13 mL pentane was added to a reddish brown solution of $Fe(CO)_4(\eta^1$-dppm) (74mg, 0.134 mmol) in 6 mL CH_2Cl_2 which resulted in the formation of a reddish brown suspension. The mixture was then stirred under a slow stream of N_2 at room temperature for 43 h. The solvent was then removed under vacuum. Recrystallization from CH_2Cl_2/pentane gave **20** as a yellow solid (104 mg, 90%). Anal.Calcd. for $C_{35}H_{22}O_6P_2F_6FeRu$: C, 48.24; H, 2.54. Found: C, 48.15; H, 2.68.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2084w, 2024s, 2012s, 1976m; ; $\upsilon_{C=C}$: 1603 w.

^1H NMR: 3.58 (t, $^2J_{PH}$ = 10.27 Hz).

$^{31}P\{^1H\}$ NMR: 63.7 (dq, $^2J_{PP}$ = 100.4 Hz, $^4J_{PF}$ = 1.9 Hz, P-Fe), 33.5 (dq, $^2J_{PP}$ = 100.4 Hz, $^4J_{PF}$ = 6.2 Hz, P-Ru).

^{19}F NMR: - 55.5 (dq, $^4J_{FF}$ = 13.7 Hz, $^4J_{PF}$ = 6.2 Hz), - 56.9 (dq, $^4J_{FF}$ = 13.7 Hz, $^4J_{PF}$ = 1.9 Hz).

$^{13}C\{^1H\}$ NMR: 208.1 (s), 45.8 (t, $^2J_{CP}$ = 27.6 Hz, $PPh_2CH_2PPh_2$).

Characterization of $FeRu(CO)_6\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2(CF_3)_2\}(\mu\text{-dppm})$, 19

^1H NMR: 4.18 (ddd, $^2J_{HH}$ = 13.22 Hz, $^2J_{PH}$ = 12.56 Hz, $^2J_{PH}$ = 11.48 Hz, 1H), 3.33 (ddd, $^2J_{HH}$ = 13.22 Hz, $^2J_{PH}$ = 12.43 Hz, $^2J_{PH}$ = 12.73 Hz, 1H).

$^{31}P\{^1H\}$ NMR: 43.3 (dq, $^2J_{PP}$ = 55.2 Hz, $^4J_{PF}$ = 5.3 Hz, P-Fe), 20.0 (d, $^2J_{PP}$ = 55.2 Hz, P-Ru).

^{19}F NMR: - 53.3 (q, $^5J_{FF}$ = 12.8 Hz), - 55.5 (m, $^5J_{FF}$ = 12.8 Hz, $^4J_{PFeF}$ = 5.3 Hz).

Characterization of $FeRu(CO)_7\{\eta^2\text{-}C_2(CF_3)_2\}(\mu\text{-dppm})$, 21

$^{31}P\{^1H\}$ NMR: 66.4 (d, $^2J_{PP}$ = 36.2 Hz), 25.7 (dm, $^2J_{PP}$ = 36.2 Hz, $^4J_{PF}$ = 1.5 Hz)

^{19}F NMR: - 54.4 (d, $^4J_{PF}$ = 1.5 Hz)

5.5. References

(1) Gagne, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561.

(2) Burn, M. J.; Kiel, G.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850.

(3) Takats, J. *J. Cluster Sci.* **1992**, *3*, 479.

(4) Washington, J. Ph. D. Thesis, University of Alberta, 1994.

(5) Jonson, K. A.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1991**, *113*, 5097.

(6) Johnson, K. A.; Gladfelter, W. *Organometallics* **1992**, *11*, 2534.

(7) Mirza, H. A.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1994**, *13*, 3063.

(8) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1987**, 662.

(9) Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1509.

(10) Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc* **1987**, 3079.

(11) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1185.

(12) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 741.

(13) Kiel, G.; Takats, J. *Organometallics* **1989**, *8*, 839.

(14) Hogarth, G.; Lavender, M. H. *J. Chem. Soc., Dalton Trans.* **1992**, 2759.

(15) Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L.; Hogarth, G. *Polyhedron* **1995**, *14*, 2723.

(16) Antwi-Nsiah, F.; Cowie, M. *Organometallics* **1992**, *11*, 3157.

(17) Cano, M.; Heras, J. V.; Pinilla, P. O. E. *J. Organomet. Chem.* **1991**, *410*, 101.

(18) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press Inc.: New York, 1981, pp 151-182.

(19) Bond, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.

(20) Jablonski, C. R.; Wang, Y. *Inorg. Chem.* **1982**, *21*, 4037.

(21) Atwood, J. D.; Wovkulich, M. J.; Sonnenberger, D. C. *Acc. Chem. Res.* **1983**, *16*, 350.

(22) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.

(23) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155.

(24) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

(25) Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. *J. Chem. Soc., Dalton Trans.* **1976**, 953.

(26) Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1331.

(27) Jablonski, C. R.; Wang, P. *Organometallics* **1985**, *4*, 465.

(28) Wright, G.; Glyde, R. W.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1973**, 220.

(29) Cotton, F. A.; Frenz, B. A.; Shaver, A. *Inorg. Chim. Acta* **1973**, *7*, 161.

(30) Zumdahl, S. S.; Drago, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 6669.

(31) Benson, J. W.; Keiter, R. L. *J. Organomet. Chem.* **1995**, *495*, 77.

(32) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777.

(33) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(34) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(35) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

(36) Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2751.

(37) Casey, C. P.; Carino, R. S.; Hayashi, R. K.; Schladetzky, K. D. *J. Am. Chem. Soc.* **1996**, *118*, 1617.

(38) McDonald, R. Ph. D. Thesis, University of Alberta, 1991.

(39) Jenkins, J. A.; Cowie, M. *Organometallics* **1992**, *11*, 2767.

(40) Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun.* **1979**, 277.

(41) Dickson, R. S.; Fallon, G. D.; Jenkins, S. M.; Nesbit, R. J. *Organometallics* **1987**, *6*, 1240.

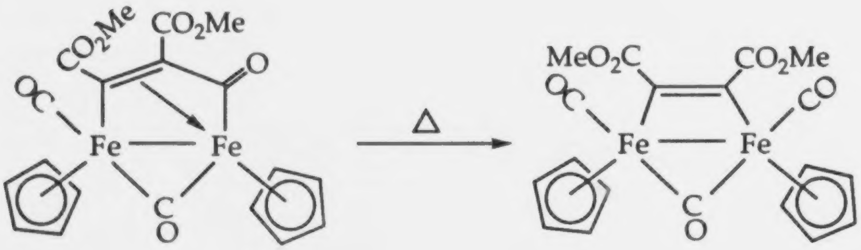
(42) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

Chapter 6

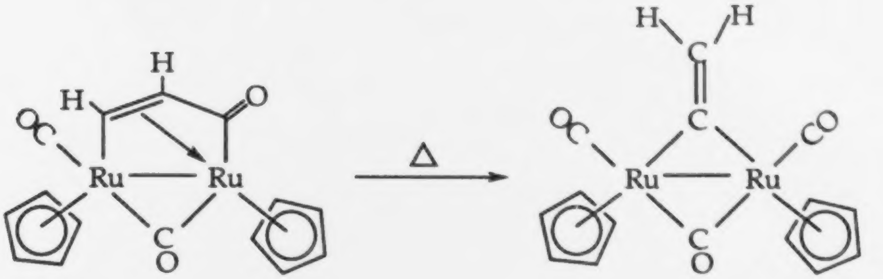
Reactivity of Metallacycles

6.1. Introduction

As described in Chapter 1, metallacycles are involved in numerous organic reactions mediated by transition metal compounds.[1-8] Two important classes of such compounds, which are closely related to those described in the previous Chapters, are dimetallacyclopentenones and metallacyclobutenones. Dimetallacyclopentenone complexes containing iron and ruthenium have been extensively studied.[9-13] The ease of carbon-carbon bond formation is elegantly exemplified by stepwise formation of a diiron tropone complex *via* a diferracyclopentenone compound as an intermediate.[14] Rich organic chemistry at dinuclear centers has also been revealed in a variety of thermal rearrangements, leading to dimetallacyclobutenes[11,15] and bridging vinylidenes (eqs. 6.1- 6.2).[10,16,17]

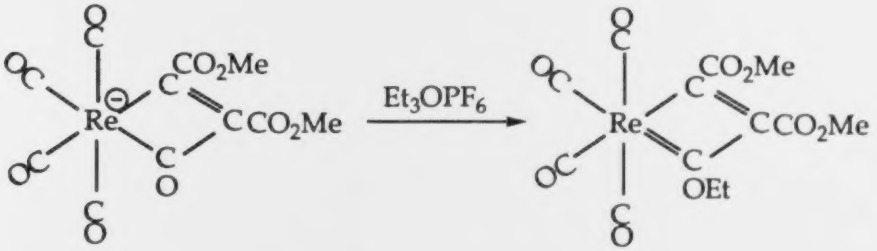


(6.1)



(6.2)

In contrast to homonuclear systems, relatively little is known about the organic chemistry of heterometallic complexes. It was, therefore, of interest to investigate the reactivity of heterodimetallacyclopentenone complexes such as compound **13**. While dimetallacyclopentenone complexes have attracted much attention, it is perhaps surprising that there are only a few known examples of simple mononuclear metallacyclobutenone complexes.[18-20] Wojcicki[21,22] and Chetcuti[23] recently reported that metallacyclobutenone complexes are prone to undergo electrophilic addition to yield metallacyclobutadiene complexes (eq. 6.3). Such complexes are of interest in that they are related to Fischer carbene complexes which have been widely used in organic synthesis.[24-27] These studies prompted us to examine the reactivity of osmacyclobutenone **10a** and osmacyclopentenedione **12** towards electrophiles. The results of alkylation of **10a** and **12** and thermolysis of **13** are described in this Chapter.

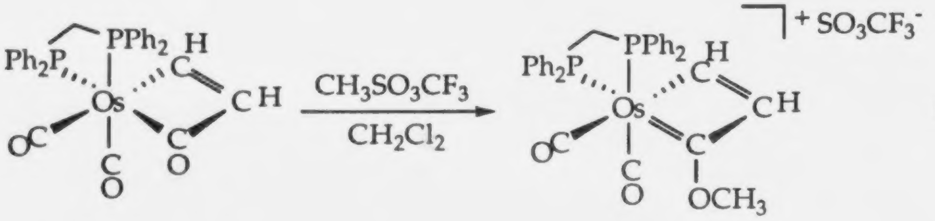


(6.3)

6.2. Results and Discussion

6.2.1. Alkylation of $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (10a) and $Os(CO)_2\{\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta^2\text{-dppm})$ (12)

When compound **10a** was treated with methyl triflate in dichloromethane, the new compound $[Os(CO)_2\{\eta^2\text{-}CHCHC(OMe)\}(\eta^2\text{-dppm})][SO_3CF_3]$(**22**) was obtained in 86% yield (eq 6.4).

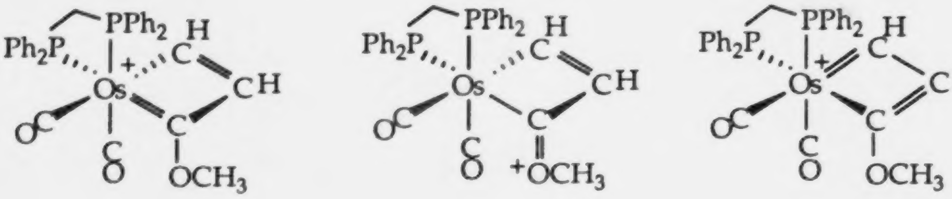


(6.4)

10a **22**

Compound **22** was characterized by IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The IR spectrum of **22** contains two terminal CO stretching bands at 2045 and 1989 cm^{-1}, both bands are at higher frequencies with respect to the terminal CO stretches of compound **10a**. This indicates less back-bonding from the metal d orbitals to the carbonyls, which is consistent with the formation of a cationic species. In the ^1H NMR spectrum, three resonances at δ 9.12, 7.90, and 4.68 in a ratio of 1:1:3 are assigned to the protons of the osmacyclobutadiene ring and methoxy group, respectively. The $^{31}P\{^1H\}$ NMR spectrum showed two resonances at δ - 45.5 and - 50.2, which are at higher field than that of free dppm and indicate that the four-membered chelating dppm ring remains unchanged.[28,29] In the $^{13}C\{^1H\}$ NMR spectrum the low field doublet of doublets at δ 234.2 ($^2J_{CP}$ = 61 Hz, $^2J_{CP}$ = 9 Hz) is assigned to the carbene carbon as the chemical shifts of

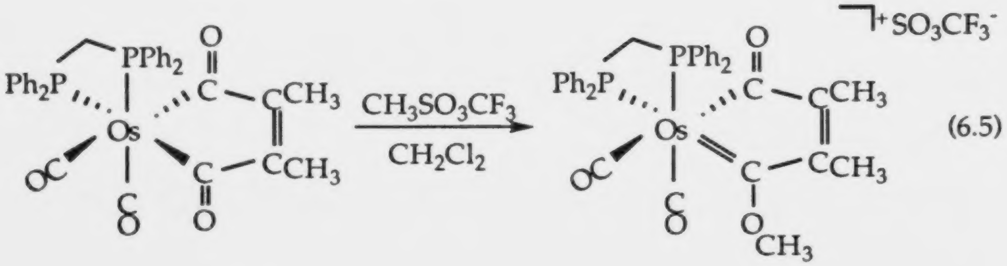
Fischer carbene carbons are in the range from 200 ppm to 400 ppm.[30] The $^{13}C\{^1H\}$ NMR spectrum, obtained by starting with a ^{13}CO enriched sample of **10a**, where the acyl carbon was also enriched, showed this resonance to be the same intensity as those of the terminal CO resonances and indicated that the carbene carbon at δ 234.2 comes from the acyl group of compound **10a**. The coupling constants of 61 Hz and 9 Hz are due to the *trans* and *cis* couplings between phosphorus and the carbene carbon. These data are in accord with the proposed structure for **22**. Further confirmation came from an APT experiment which showed that the resonances at δ 181.4 and 160.8 were clearly due to carbons bonded to one hydrogen. In comparison with **10a**, the chemical shift of the β-carbon has moved to lowfield by 15 ppm whereas the carbon originating from the acyl group in **10a** has moved downfield by 35 ppm. The remaining resonances at δ 180.0 ($^2J_{CP}$ = 89.8 Hz, $^2J_{CP}$ = 6.7 Hz) and 181.7 are characteristic of terminal carbonyls bonded to osmium.[31] As shown in Scheme 6.1, there are three possible resonance structures. The disappearance of the acyl band in the IR spectrum suggests that resonance structure L' does not make a significant contribution to the bonding, whereas the ^{13}C NMR data indicate that both K' and M' appear to contribute to the bonding where K' is the major contributor. Thus, the IR and NMR spectroscopic data are consistent with the resonance structures K' and M' whereas resonance forms L' does not make a significant contribution to the bonding in compound **22** .



K' **L'** **M'**

Scheme 6.1

Although compound **12** has two potential reaction sites, the alkylation reaction, even with excess methyl triflate, occurs only at one site to yield the corresponding alkylation product $[Os(CO)_2\{\eta^2\text{-}C(O)C_2(Me)_2C(OMe)\}(\eta^2\text{-dppm})][SO_3CF_3]$ (**23**) (eq 6.5).



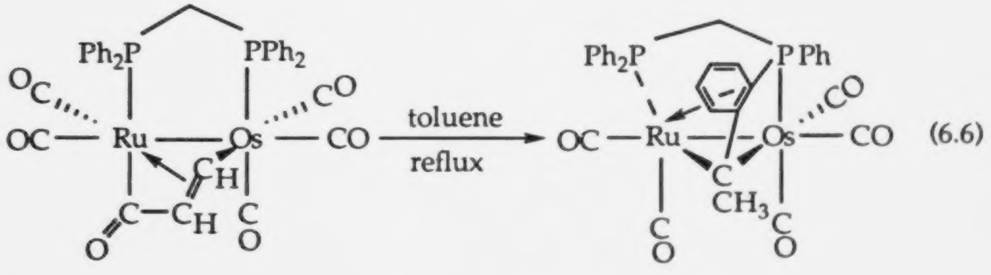
(6.5)

12 **23**

Based on the spectroscopic similarity between compound **22** and compound **23**, the characterization of **23** is straightforward. The $^{13}C\{^1H\}$ NMR spectrum shows one low field signal for the carbene carbon at δ 286.4 ($^2J_{CP}$ = 55.8 Hz, $^2J_{CP}$ = 7.5 Hz); the coupling constants of 55.8 Hz and 7.5 Hz indicate that the carbene carbon is *trans* to one phosphorus atom and *cis* to the other. Consistent with the alkylation occurring at the acyl group *trans* to the equatorial phosphine, the chemical shift of remaining acyl group at δ 238.8 ($^2J_{CP}$ = 11.9 Hz, $^2J_{CP}$ = 6.3 Hz) is similar to that of compound **12** and the coupling constants are in accord with its *cis* disposition to both phosphines. Two resonances at δ 182.6 ($^2J_{CP}$ = 9.3 Hz) and 177.8 ($^2J_{CP}$ = 67.1 Hz, $^2J_{CP}$ = 8.3 Hz) are due to the terminal carbonyls.[31] The resonance at δ 177.8 exhibits strong phosphorus coupling indicating that it is *trans* to the axial phosphine. The two remaining ring carbons resonate at δ 179.9 and 165.1, both resonances showed additional couplings to hydrogens in the ^1H coupled spectrum. All other features of the IR, ^1H, and $^{31}P\{^1H\}$ NMR spectra of compound **23** closely resemble those of compound **22**. Thus the compound **23** is formulated as shown in eq 6.5.

6.2.2. Thermolysis of $OsRu(CO)_5\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (13)

Compound **13** is stable in solution at room temperature. However, when it is heated in refluxing toluene, it gradually converts to a single product. In light of the structure of $Fe_2(CO)_5\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4C(CH_2Ph)\}$ obtained from thermolysis of the analogous $Fe_2(CO)_5\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$,[32] product **24** was identified as shown in eq 6.6.



13 **24**

The formulation of compound **24** is based on extensive spectroscopic studies including ^{13}C labelling experiment. The IR spectrum of **24** exhibited four terminal carbonyl bands at 2043, 1986, 1952, and 1926 cm^{-1}. More importantly, one band is also observed at 736 cm^{-1} and is characteristic of the C-H out-of-plane deformation of an ortho-disubstituted benzene.[33,34] In the ^{1}H NMR spectrum of **24**, three resonances at δ 5.55, 4.38, and 3.25, in a ratio of 1:1:3, are assigned to the two inequivalent methylene protons of the bridging dppm ligand and a methyl group, respectively. The $^{31}P\{^{1}H\}$ NMR spectrum showed two doublets at δ 30.3 and - 3.6. The former resonance is attributed to the Ru-bound phosphorus nucleus whereas the latter is due to the Os-bound phosphorus.[35] It is noteworthy that, in contrast to the chemical shifts of compound **13**, the chemical shift of the Ru-bound phosphorus is not changed significantly while that of Os-bound phosphorus is shifted to higher field by 12 ppm, consistent with orthometalation taking place at the osmium center.[36] As shown in Figure 6.1(a), the $^{31}C\{^{1}H\}$ NMR spectrum of **24** displays five terminal carbonyl resonances at δ 205.8, 197.1, 186.5, 185.3, 178.7. No other signals are observed in the region from 200 ppm to 700 ppm. Selective decoupling of the higher field, Os-bound, phosphorus resonance leads to collapse of the three doublets at δ 186.5, 185.3, and 178.7 into singlets, while the doublet of doublets at δ 197.1 is simplified to a doublet (Fig 6.1 (c)). Similarly, selective decoupling of the other phosphorus resonance at δ 30.3 leads to the collapse of the doublet of doublets at δ 197.1 into a doublet while the other resonances remain unchanged, Fig 6.1(d). This demonstrates that the resonances at δ 186.5, 185.3, and 178.7 are due to the carbonyls bound to the osmium center while the other two signals at δ 205.8 and 197.1 are attributed to those on ruthenium. In addition, the

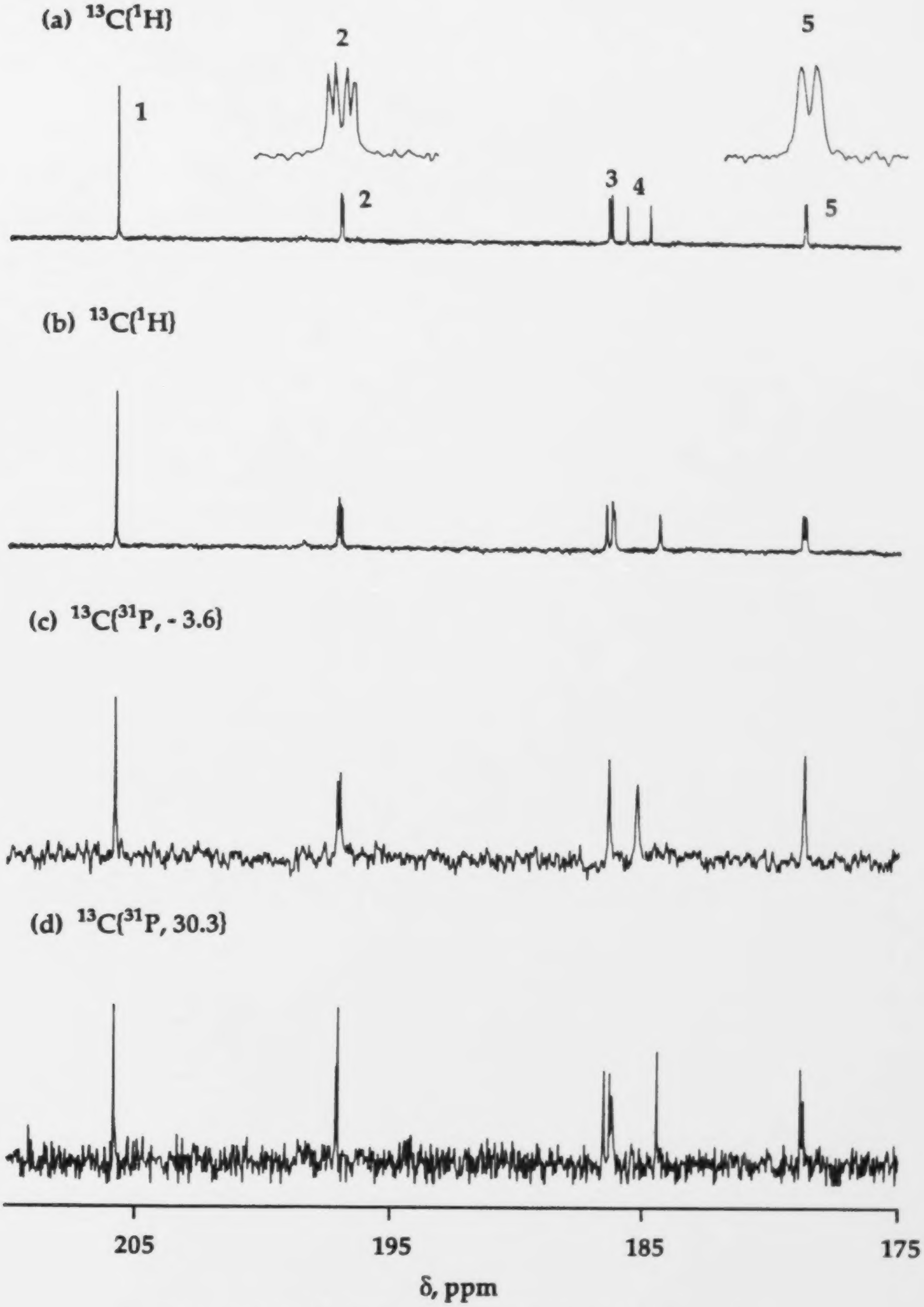
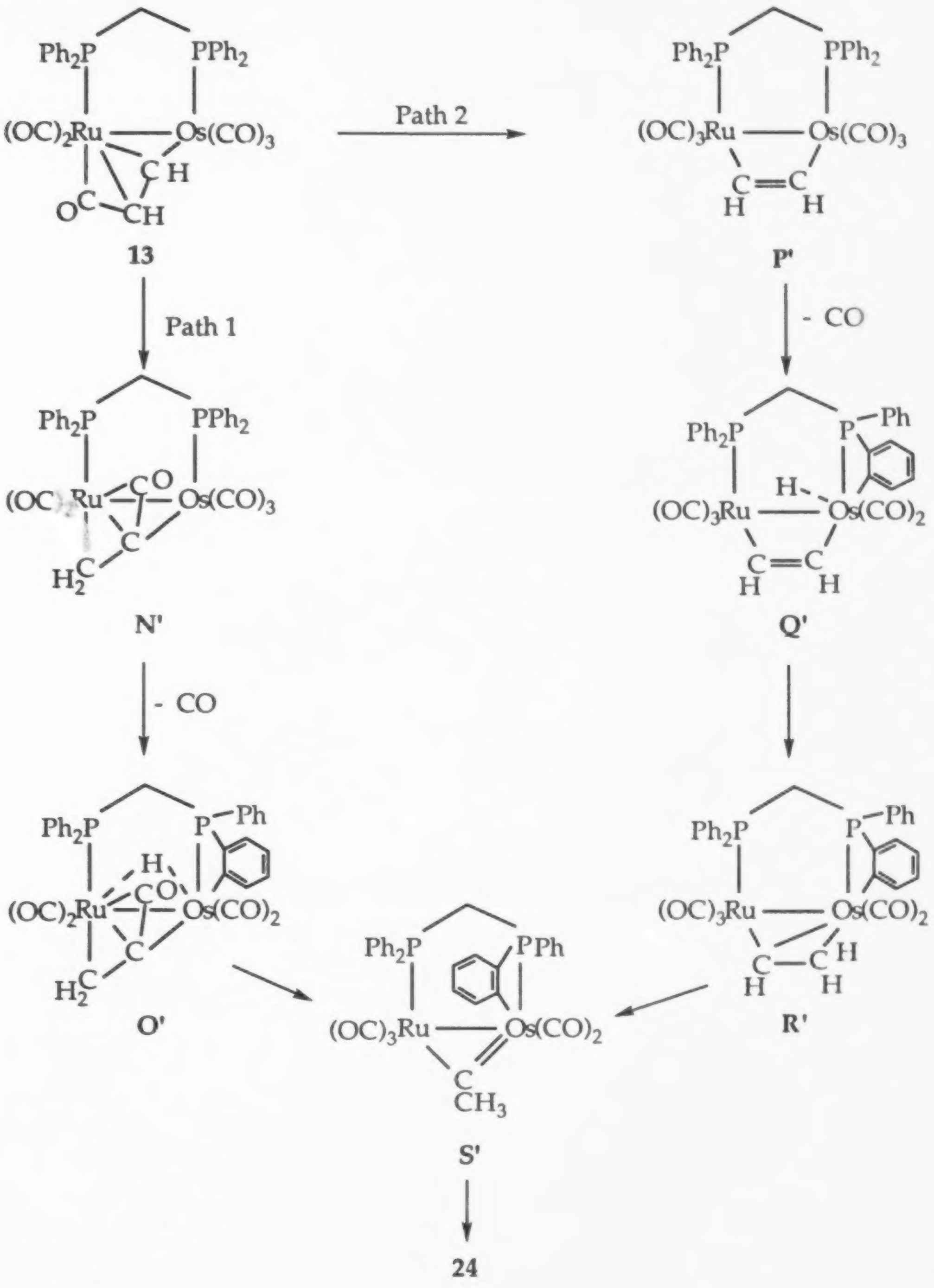


Figure 6.1: $^{13}C\{^1H\}$ and $^{13}C\{^{31}P\}$ NMR Spectra of 24:
Spectrum (a) at 100.614 MHz; Spectra (b), (c), and (d) at 50.323 MHz

strong coupling (91.1 Hz) between the carbonyl at δ 185.3 and the high field phosphorus resonance indicates that they are in *trans* positions, whereas the other carbonyls are *cis* to the phosphorus nuclei as can be deduced from their small coupling constants. The methyl group signal was observed at δ 34.1 and was confirmed by its quartet appearance in the ^1H coupled spectrum. The $^1J_{CH}$ of 126.2 Hz is similar to that of ethane.[37] In order to identify the carbyne carbon, the preparation of compound **24** was carried out using compound **13** in which the alkene unit in the (C_2H_2CO) group was enriched in ^{13}C (compound **13** was prepared from $Ru(CO)_4(\eta^1\text{-dppm})$ and $Os(CO)_4(\eta^2\text{-}^{13}C_2H_2)$). The corresponding $^{13}C\{^1H\}$ NMR spectrum of **24** ($^{13}C_2$) showed two doublets of doublets at δ 130.0 and 34.1; the signal at 34.1 is at the same position as observed in unenriched **24** ($^1J_{CC}$ = 36 Hz). The values of chemical shift are similar to those (δ 143.4 and 47.0) found in $Fe_2(CO)_5\{\mu\text{-}Ph_2PCH_2P(Ph)C_6H_4C(CH_2Ph)\}$.[32] The $^1J_{CC}$ coupling constant is similar to that of ethane (34.6 Hz).[37] Selective decoupling of the phosphorus at δ 30.3 leads to collapse of these signals into two doublets, while decoupling the other ^{31}P at δ - 3.6 does not affect these signals. This is consistent with the CCH_3 unit being approximately *trans* to the phosphorus on ruthenium and *cis* to the phosphorus on osmium. The molecular structure of $Fe_2(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ shows that this is indeed the case.

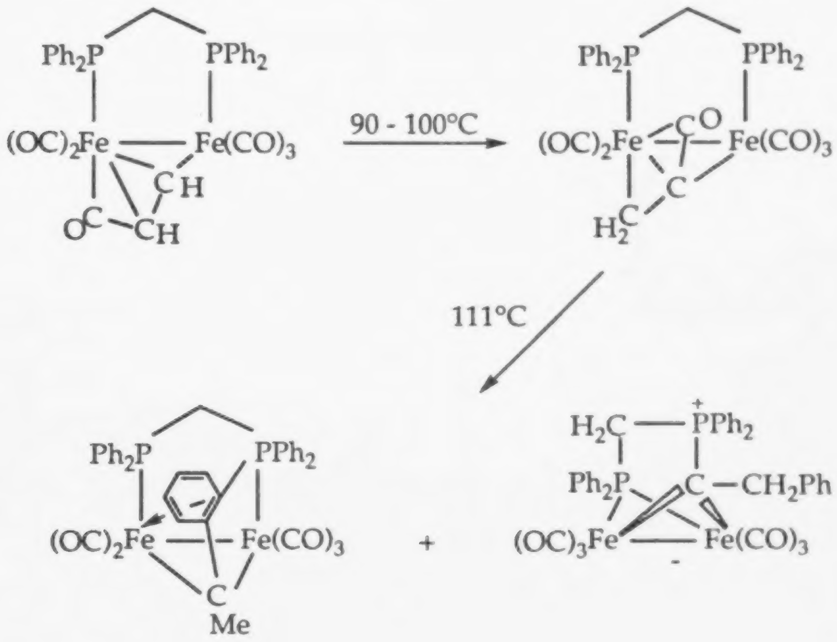
Proposed Pathways for Formation of 24. Two reasonable pathways are proposed for conversion of the dimetallacyclopentenone species **13** to alkylidyne compound **24** (Scheme 6.2). Path 1 is initiated by a 1,2-hydrogen shift to give intermediate N', which undergoes CO dissociation, presumably at the ruthenium center because of the weaker Ru-CO bond,[38]


13
Path 2
P'
Path 1
- CO
N'
Q'
- CO
O'
R'
S'
24

Scheme 6.2: Proposed Mechanism for Formation of 24 followed by CO migration from osmium to ruthenium and orthometalation at the osmium center to generate species O'. This intermediate undergoes further transfer of the hydride to the methylene carbon and carbonyl rearrangement to give bridging alkylidyne species S'. Finally, carbon-carbon bond formation between the alkylidyne carbon and the orthometallated carbon generates complex **24**. Path 2 involves initial decarbonylation to give a dimetallacyclobutene species P'; such a process has precedent.[11] Species P' undergoes CO dissociation, again presumably at the ruthenium center, followed by CO migration from osmium to ruthenium and orthometallation at the osmium center to give species Q'. This species undergoes hydride transfer to give the vinyl species R'. Further 1,2-hydrogen shift and carbonyl rearrangement yield bridging alkylidyne species S', followed by carbon-carbon bond formation to afford complex **24**.

The common features for both pathways are the 1,2-hydrogen shift and the orthometallation steps. The 1,2-hydrogen shift in complexes containing either $\{\mu\text{-}\eta^1\text{:}\eta^3\text{-CHCHC(O)}\}$ group or $(\mu\text{-}\eta^1\text{:}\eta^2\text{-CHCH}_2)$ group is known.[39,40] It is also well documented that triphenylphosphine frequently undergoes C-H bond cleavage of a phenyl ring to form a cyclometallation products.[41] Although orthometallation reactions involving dppm are much less common, there is increasing evidence demonstrating that such processes are possible.[42-44]

In the thermolysis of the analogous $\text{Fe}_2(\text{CO})_5(\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_2\text{H}_2\text{CO})\}(\mu\text{-dppm})$ complex, Hogarth reported that a complex analogous to N' is formed by 1,2-hydrogen shift at 90°C before the orthometallation step takes place at 111°C (Scheme 6.3).[45,46] Based on the similarities between the two reactions, we believe that Path 1 is more likely operative in the present case as well, although Path 2 can not be ruled out.



Scheme 6.3

6.3. Conclusions

Both osmacyclobutenone **10a** and osmacyclopentenedione **12**, undergo facile alkylation with $CH_3SO_3CF_3$ to give the corresponding Fischer-type carbene complexes (**22** and **23**). The dimetallacyclic complex **13** converts to complex **24** at high temperatures by a sequence of steps involving interesting C-C and C-H bond cleavage and formation. Future studies should be directed toward the reactions of the dimetallacycles with electrophiles. Thus protonation of **13** could give the corresponding cationic dinuclear vinyl complexes, which ought to have rich derivative chemistry.[10,12,13,46]

6.4. Experimental Section

6.4.1. Starting Materials and Reagents

$Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (**10a**) and $Os(CO)_2\{\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta^2\text{-dppm})$ (**12**) were prepared as reported in Chapter 3. Methyl triflate was purchased from Aldrich Chemical Co..

6.4.2. Synthetic Procedures

Synthesis of $[Os(CO)_2\{\eta^2\text{-}CHCHC(OMe)\}(\eta^2\text{-dppm})][SO_3CF_3]$, 22

To a methylene chloride solution (5 mL) of $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (**10a**) (16 mg, 0.0234 mmol) was added 2.6 μL (0.0234 mmol) methyl triflate with a gas-tight syringe. The color of the solution gradually changed from yellow to orange over 40 min. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2/pentane to give 17 mg (86%) of an orange solid (**22**). Anal. Calcd for $C_{32}H_{27}F_3O_6P_2SOs$: C, 45.28; H, 3.21. Found: C, 44.73; H, 3.21.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2045 (s), 1989 (s).

^1H NMR: 9.12 (dd, $^3J_{HH}$ = 6.4 Hz, $^3J_{HP}$ = 2.1 Hz, Os-C*H*), 7.90 (ddd, $^3J_{HH}$ = 6.4 Hz, $^4J_{HP}$ = 3.8 Hz, $^4J_{HP}$ = 3.7 Hz, Os-CHC*H*), 5.52 (ddd, $^2J_{HH}$ = 16.5 Hz, $^2J_{HP}$ = 9.5 Hz, $^2J_{HP}$ = 9.5 Hz, $Ph_2PC\mathit{H}_2PPh_2$), 5.29 (ddd, $^2J_{HH}$ = 16.5 Hz, $^2J_{HP}$ = 9.2 Hz, $^2J_{HP}$ = 9.3 Hz, $Ph_2C\mathit{H}_2PPh_2$), 4.68 (s, $OC\mathit{H}_3$).

$^{31}P\{^1H\}$ NMR: - 45.5 (d, $^2J_{PP}$ = 19.3 Hz), - 50.2 (d, $^2J_{PP}$ = 19.3 Hz).

$^{13}C\{^1H\}$ NMR : 234.2 (dd, $^2J_{CP}$ = 61 Hz, $^2J_{CP}$ = 9 Hz, $OsC(OCH_3)$), 180.0(dd, $^2J_{CP}$ = 89.8 Hz, $^2J_{CP}$ = 6.7 Hz, CO), 181.7 (s, CO), 181.4 (d, $^2J_{CP}$ = 12.6 Hz, OsCH), 160.8 (d, $^3J_{CP}$ = 12.0 Hz, $^3J_{CP}$ = 8 Hz, OsCHCH), 70.6 (d, $^4J_{CP}$ = 3.4 Hz, OCH_3), 46.2 (t, $^2J_{CP}$ = 31.4 Hz, $PPh_2CH_2PPh_2$).

Synthesis of $[Os(CO)_2\{\eta^2\text{-}C(O)CMeCMeC(OMe)(\eta^2\text{-dppm})][SO_3CF_3]$, 23

To a solution of compound **12** (25 mg, 0.0338 mmol) in 10 mL CH_2Cl_2 was added methyl triflate (23 μL, 0.205 mmol) with a gas-tight syringe. The resulting solution was stirred at room temperature for 18 h, during which time the color of the solution gradually changed from yellow to pale orange. The solvent was then removed in vacuo. Recrystallization from CH_2Cl_2/pentane gave 26.8 mg (88%) of an orange solid (**23**). Anal. Calcd for $C_{35}H_{31}F_3O_7P_2SOs\cdot 0.5CH_2Cl_2$: C, 45.01; H, 3.40. Found: C, 44.46; H, 3.71.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2048 s, 1998 s, 1630 w; υ_{acyl}: 1605w.

^1H NMR: 5.69 (ddd, $^2J_{HH}$ = 15.5 Hz, $^2J_{PaH}$ = 9.2 Hz, $^2J_{PbH}$ = 9.3 Hz, 1H), 5.11 (ddd, $^2J_{HH}$ = 15.5 Hz, $^2J_{PaH}$ = 12.6 Hz, $^2J_{PbH}$ = 13.1 Hz, 1H), 4.91 (s, 3H), 1.87 (m, $^5J_{PaH}$ = 0.7 Hz, $^5J_{HH}$ = 1.0 Hz, 3H), 1.27 (m, $^5J_{PaH}$ = $^5J_{HH}$ = 1.0 Hz, 3H).

$^{31}P\{^1H\}$ NMR: - 40.0 (d, $^2J_{PP}$ = 28.4 Hz, P_a), - 50.0 (d, $^2J_{PP}$ = 28.4 Hz, P_b).

$^{13}C\{^1H\}$ NMR: 286.4 (dd, $^2J_{PC}$ =55.8 Hz, $^2J_{PC}$ = 7.5 Hz, Os=C(OMe)-), 238.8 (dd, $^2J_{PC}$ = 11.9 Hz, $^2J_{PC}$ = 6.3 Hz, acyl), 182.6 (d, $^2J_{PC}$ = 9.3 Hz, 1CO), 179.9 (s, Os-C(O)-C(Me)=), 177.8 (dd, $^2J_{PC}$ = 67.1 Hz, $^2J_{PC}$ = 8.3 Hz, 1CO), 165.1 (d, $^3J_{PC}$ = 8.3 Hz, Os=C(OMe)-C(Me)=), 38.6 (dd, $^2J_{PC}$ = 30.4 Hz, $^2J_{PC}$ =34.3 Hz, $PPh_2CH_2PPh_2$), 27.5 (s, CH_3), 11.5 (d, $^4J_{PC}$ = 12.2 Hz, CH_3), 72.9 (s, OCH_3).

Thermolysis of $OsRu(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$, 13

A solution of compound **13** (115 mg, 0.397 mmol) in 5 mL toluene was refluxed for 5 h, during which time the reddish brown solution gradually turned a dark reddish brown color. The solvent was then removed in vacuo and the residue was recrystallized with CH_2Cl_2/pentane to yield 83 mg (74%) of **24** as a brown solid. MS (70 ev, 220°C, m/e): M^+ - n CO, n = 0 - 5.

IR (CH_2Cl_2, cm^{-1}): υ_{CO}: 2043 s, 1986 vs, 1952 s, 1926 m.

^1H NMR: 8.2 - 6.7 (m, Ph), 5.55 (ddd, $^2J_{HH}$ = $^2J_{P_{Os}H}$ = 14.9 Hz, $^2J_{P_{Ru}H}$ = 6.7 Hz, 1H), 4.38 (ddd, $^2J_{HH}$ = 14.9 Hz, $^2J_{P_{Ru}H}$ = 10.3 Hz, $^2J_{P_{Os}H}$ = 2.2 Hz, 1H), 3.25 (dd, $^4J_{P_{Ru}H}$ = 4.6 Hz, $^4J_{P_{Os}H}$ = 2.2 Hz, 3H).

$^{31}P\{^1H\}$ NMR: 30.3 (d, $^2J_{PP}$ = 97 Hz, P-Ru), - 3.6 (d, $^2J_{PP}$ = 97 Hz, P-Os).

$^{13}C\{^1H\}$ NMR: 205.8 (s, CO), 197.1 (dd, $^2J_{CP_{Ru}}$ = 5.6 Hz, $^2J_{CP_{Os}}$ = 2.5 Hz, 1CO), 186.5 (d, $^2J_{CP_{Os}}$ = 11.4 Hz, 1CO), 185.3 (d, $^2J_{CP_{Os}}$ = 91.1 Hz, 1CO), 178.7 (d, $^2J_{CP_{Os}}$ = 9.0 Hz, 1CO), 50.8 (dd, $^1J_{CP_{Os}}$ = 59.0 Hz, $^1J_{CP_{Ru}}$ = 19.2 Hz, $PPh_2CH_2PPh_2$), 34.1 (d, $^3J_{CP_{Ru}}$ = 2.7 Hz, CH_3). New resonances in the Ph region compared to compound **13**: 135.9 (s), 124.7 (d, $^3J_{CP_{Os}}$ = 8.4 Hz), 122.0 ($^3J_{CP_{Os}}$ = 8.4 Hz), 72.3 (d, $^2J_{CP_{Os}}$ = 52.6 Hz).

$^{13}C\{^1H\}$ NMR (with $^{13}C_2H_2$ SM): 130.0 (dd, $^1J_{CC}$ = 36.0 Hz, $^2J_{CP_{Ru}}$ = 9.1 Hz, CCH_3), 34.1 (dd, $^1J_{CC}$ = 36.0 Hz, $^3J_{CP_{Ru}}$ = 2.8 Hz, CCH_3).

^{13}C NMR (with $^{13}C_2H_2$ SM): 130.0 (dm, $^1J_{CC}$ = 36.0 Hz, CCH_3), 34.1 (ddq, $^1J_{CC}$ = 36.0 Hz, $^3J_{CP_{Ru}}$ = 2.8 Hz, $^1J_{CH}$ = 127.3 Hz, CCH_3).

^1H NMR (with $^{13}C_2H_2$ SM): 3.25 (dm, $^1J_{CH}$ = 125.0 Hz, CH_3).

Synthesis of $Os(CO)_4(\eta^2\text{-}^{13}C_2H_2)$

A pentane solution of $Os(CO)_5$ (115mg) was transferred under argon to an immersion well cooled to - 40°C and sufficient pentane was added (ca. 110 mL) to ensure that the level of the solution is above the lamp. The system was then partially placed under vacuo. Acetylene ($^{13}C_2H_2$) was admitted until approximately one atmosphere pressure of $^{13}C_2H_2$ was obtained. The solution was irradiated at this temperature for 2 h. The solution was then transferred to a round bottom flask, and the solvent was removed in vacuo at - 78°C. Sublimation to a dry-ice cooled probe gave 67 mg (58%) of $Os(CO)_4(\eta^2\text{-}^{13}C_2H_2)$ as a white solid.

6.5. References

(1) Schore, N. E. *Chem. Rev.* **1988,** *88,* 1081.

(2) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis;* John Wiley & Sons: New York, 1992, pp 191-216.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987, pp 459-520.

(4) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977,** *10,* 1.

(5) Wilke, G. *Pure Appl. Chem.* **1978,** *50,* 677.

(6) Puddephatt, R. J. *Coord. Chem. Rev.* **1980,** *33,* 149.

(7) Puddephatt, R. J. *Comments Inorg. Chem.* **1982,** *2,* 69.

(8) Lindner, E. *Adv. Heterocycl. Chem.* **1986,** *39,* 237.

(9) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980,** 803.

(10) Dyke, A. F.; Finnimore, S. R.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Riding, G. H.; Taylor, G. E. In *Reactivity of Metal-Metal Bonds*ACS Symp. Ser.: 1981; Vol. 155; pp 259-271.

(11) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982,** 1297.

(12) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983,** 1417.

(13) Knox, S. A. R. *J. Organomet. Chem.* **1990,** *400,* 255.

(14) Hogarth, G.; Kayser, F.; Knox, S. A. R.; Morton, D. A. V.; Orpen, A. G.; Turner, M. L. *J. Chem. Soc., Chem. Commun.* **1988,** 358.

(15) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Organomet. Chem.* **1984,** *272,* C45.

(16) Knox, S. A. R. *Pure & Appl. Chem.* **1984,** *56,* 81.

(17) Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Orpen, A. G.; Plaas, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2661.

(18) Burt, R.; Cooke, M.; Green, M. *J. Chem. Soc. (A)* **1970**, 2981.

(19) Herrea, A.; Hoberg, H.; Mynott, R. *J. Organomet. Chem.* **1981**, *222*, 331.

(20) Hoberg, H.; Herrera, A. *Angew. Chem. Int., Ed. Engl.* **1981**, *20*, 876.

(21) Padolik, L. L.; Gallucci, J.; Wojcicki, A. *J. Organomet. Chem.* **1990**, *383*, C1.

(22) Padolik, L. L.; Callucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 9986.

(23) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1995**, *14*, 2937.

(24) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1.

(25) Hegedus, L.; Imwinkelried, R.; Alarid-Sargent, M.; Cvorak, D.; Yoshitaka, S. *J. Am. Chem. Soc.* **1990**, *112*, 1109.

(26) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(27) Dotz, K. H. *New J. Chem.* **1990**, *14*, 433.

(28) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(29) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

(30) Dotz, K. H.; Fischer, H.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983.

(31) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press Inc.: New York, 1981, pp 151-182.

(32) Hogarth, G. Ph. D. Thesis, University of Bristol, 1986.

(33) Hata, G.; Kondo, H.; Miyake, A. *J. Am. Chem. Soc.* **1968**, *90*, 2278.

(34) Valentine, J. S. *J. Chem. Soc., Chem. Commun.* **1973**, 857.

(35) Antonelli, D. M. Ph. D. Thesis, University of Alberta, 1991.

(36) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. (A)* **1971**, 3833.

(37) Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley-Interscience, John Wiley & Sons, Inc.: New York, 1972, pp 28-29.

(38) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(39) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(40) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 60.

(41) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In University Science Books: Mill Valley, CA, 1987; pp 298-300.

(42) Jeffery, J. C.; Orpen, A. G.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1986**, 173.

(43) Bergounhou, C.; Bonnet, J.; Fompeyrine, P.; Lavigne, G.; Lugan, N.; Mansilla, F. *Organometallics* **1986**, *5*, 60.

(44) Hilts, R. W.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 1297.

(45) Hogarth, G.; Knox, S. A. R.; Lloyd, B. R.; Morton, D. A. V.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 360.

(46) Doherty, N. M.; Howard, J. A. K.; Knox, S. A. R.; Terrill, N. J.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1989**, 638.

Chapter 7

Conclusions

The objective of this thesis was to obtain a better understanding of the reactivity features of $M(CO)_4(\eta^2\text{-alkyne})$ (M = Ru, Os) species, namely, the roles of these species in the formation of dimetallacycles. The $M(CO)_4(\eta^2\text{-alkyne})$ complexes seem to be simple, yet their reactions with other metal carbonyls frequently reveal surprising results.[1-4] Therefore, the approach used was to first investigate the reactions of these species with simple monophosphines. As described in Chapter 1, this was of interest as it could provide a basis for understanding the unusual and interesting condensation reactions of $M(CO)_4(\eta^2\text{-alkyne})$ with other eighteen-electron species $M(CO)_5$ and $(C_5R_5)M'(CO)_2$ (R = H, Me; M' =Co, Rh, Ir), resulting in the formation of dimetallacycles.[1-4] The second project was to examine the reactions with diphosphines (e.g., dppm, dmpm, dppe, and dmpe). The reactions with dppm were of particular interest since the products obtained were expected to be suitable precursors for synthesis of dinuclear complexes.[5,6] We were also interested in the reactions with $M(CO)_4(\eta^1\text{-dppm})$ (M = Fe, Ru) in order to closely mimic the condensation reactions between $M(CO)_4(\eta^2\text{-alkyne})$ and other metal carbonyls. It was hoped that the presence of a dppm ligand in $M(CO)_4(\eta^1\text{-dppm})$ would allow the observation of some intermediates in the condensation reactions. Finally, the reactivity of the metallacycles obtained was investigated in order to further understand the properties of these complexes.

Reactions of $M(CO)_4(\eta^2\text{-alkyne})$ with monophosphines generated two types of products (Chapter 2). With electron poor alkynes (e.g., CF_3C_2H and $CF_3C_2CF_3$), both monosubstituted and disubstituted products were obtained. On the other hand, in the case of electron rich alkynes (e.g., C_2H_2 and $C_2(Me)_2$), in addition to CO substitution, CO insertion products were also observed. Reactions with diphosphines (e.g., dppm, dmpm, dppe, and dmpe) (Chapter 3) are also consistent with this general trend, except that $Ru(CO)_4(\eta^2\text{-HFB})$ reacted with dppm and dmpm to form the unusual metallacyclic complexes $(OC)_3Ru\text{-}P(R_2)(CH)\text{-}P(R_2)\text{-}C(CF_3)\text{-}C(H)(CF_3)$ (R = Ph, **8a**; Me, **8b**), in which the phosphine ligand has linked with the alkyne carbon. To our knowledge, the CO inserted complexes $Os(CO)_2(PMe_3)_2\{\eta^2\text{-}C(O)C_2H_2)\}$ (**4a**, **4b**), $Os(CO)_3\{P(t\text{-}C_4H_9)_3\}\{\eta^2\text{-}C(O)C_2R_2C(O)\}$ (R = Me, **5a**; H, **5b**), $Os(CO)_2\{\eta^2\text{-}C(O)CHCH\}(\eta^2\text{-dppm})$ (**10a**, **10b**), and $Os(CO)_2\{\eta^2\text{-}C(O)C(CH_3)C(CH_3)C(O)(\eta^2\text{-dppm})$ (**12**), are the first clear examples of coupling between coordinated CO and coordinated alkyne ligand in a mononuclear complex.

Although the reactions are strongly dependent on the nature of the coordinated alkyne, they all appear to proceed by initial CO substitution. As described in Chapter 1, the facile CO dissociation from $M(CO)_4(\eta^2\text{-alkyne})$ is attributed to a combination of four electron destabilization in the ground state and four electron stabilization in the putative $M(CO)_3(\eta^2\text{-alkyne})$ intermediate. The manifestation of the four electron interactions is also seen in subsequent steps of the reactions where either facile CO insertion or further CO substitution takes place. This can be explained by comparing the $M(CO)_3(PR_3)(\eta^2\text{-alkyne})$ and $M(CO)_4(\eta^2\text{-alkyne})$ complexes in terms of phosphine effects. In the phosphine substituted $M(CO)_3(PR_3)(\eta^2$-alkyne) derivatives, the four electron ground state destabilization is expected to be stronger than in $M(CO)_4(\eta^2$-alkyne) compounds. This will result in weakened metal-to-carbonyl and metal-to-alkyne bonding thereby facilitating both further CO substitution and CO insertion reactions. However the more electron rich nature of the metal in the phosphine substituted derivatives is also expected to enhance metal-to-ligand backbonding and oppose the effects of the four electron destabilization. It appears that metal-to-alkyne backbonding dominates in $M(CO)_3(PR_3)(\eta^2\text{-}CF_3C_2CF_3)$ complexes containing the strongly electron withdrawing hexafluorobutyne, as migratory CO insertion into the metal-alkyne bond does not take place (or does so only very slowly) due to the strong metal-alkyne bonding. Since, in the case of electron rich alkynes, facile CO insertion reactions occur following phosphine substitution, four electron destabilization and weakened metal-to-alkyne bonding is the more important factor. Although electronic factors apparently play an important role in both CO substitution and CO insertion reactions, evidence of steric effects is also seen as double CO insertion takes place in the reactions of $M(CO)_4(\eta^2\text{-}C_2R_2)$ with bulky P(t-Bu)$_3$ to yield $Os(CO)_3P(^tBu)_3\{\eta^2\text{-}C(O)C_2R_2C(O)\}$ (R = Me, **5a**; H, **5b**). In order to fully understand the nature and mechanisms of these reactions, kinetic studies and theoretical calculations in collaborations with Professors R. B. Jordan and M. A. Klobukowski of this Department are currently underway.

As expected, most CO substitution and CO insertion products are stable at room temperature due to either the strengthening of the metal-CO bonds or the elimination of four electron destabilizing interactions, but it is interesting to note that $Os(CO)_2(PMe_3)_2(\eta^2\text{-}C_2H_2)$ and $Os(CO)_3(PMe_3)(\eta^2$-

C_2H_2) undergo further transformations at room temperature. While the former compound undergoes an intramolecular oxidative addition reaction to give an acetylide hydride product, $Os(CO)_2(PMe_3)_2(H)(C_2H)$ (**6**), the latter species forms a novel dimetallacyclic product, $Os_2(CO)_5(PMe_3)_2\{\mu\text{-}\sigma{:}\eta^2\text{-}C_2H_2C(O)C_2H_2\}$ (**7**). It is noteworthy that, in the later case, facile C-C bond formation between two-metal sites takes place.

Perhaps the most noteworthy feature of these studies is that a strong correlation was found between the reactions of $M(CO)_4(\eta^2\text{-alkyne})$ compounds with $M''(CO)_4(\eta^1\text{-dppm})$ (M" = Fe, Ru) (Chapter 5) and their reactions with the other metal carbonyls, $M(CO)_5$ and $(C_5R_5)M'(CO)_2$ (R = H, CH_3; M' =Co, Rh, Ir).[1-4] In the case of electron rich alkynes, the condensation reactions give dimetallacyclopentenones while, for electron poor alkynes, dimetallacyclobutenes are formed.[1-4] Thus, reactions of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with $M''(CO)_4(\eta^1\text{-dppm})$ (M" = Fe, Ru) generated the corresponding dimetallacyclopentenones, $OsRu(CO)_5\{\mu\text{-}\eta^1{:}\eta^3\text{-}CHCHC(O)\}(\mu\text{-dppm})$ (**13**) and $FeOs(CO)_6\{\mu\text{-}\eta^1{:}\eta^1\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (**18**), whereas the reaction of $Ru(CO)_4(\eta^2\text{-HFB})$ with $Fe(CO)_4(\eta^1\text{-dppm})$ resulted in the formation of dimetallacyclobutenes $FeRu(CO)_6\{\mu\text{-}C_2(CF_3)_2\}(\mu\text{-dppm})$ (**19, 20**).

In an attempt to investigate the possible role of metallacyclobutenone species in the formation of dimetallacyclopentenones, reactions of the osmacyclobutenone species, $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (**10a**), with $Ru(CO)_4(\eta^2\text{-}C_2H_4)$ and $CpRh(CO)_2$ were carried out (Chapter 4). These reactions generated the corresponding dimetallacyclopentenone complexes, $OsRu(CO)_5\{C_2H_2C(O)\}(dppm)$ (**13**) and $CpRhOs(CO)_3\{\mu\text{-}\eta^1{:}\eta^1\text{-}CHCHC(O)\}(\mu\text{-}$

dppm) (**14**). This indicates that metallacyclobutenone species may be involved in the condensation reactions.

Another important theme of these studies was to identify reaction intermediates by monitoring the reactions at low temperatures using ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. One of the most interesting findings was discovered while monitoring the formation of compound **13** from the reaction of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with $Ru(CO)_4(\eta^1\text{-dppm})$ (Chapter 5). Consistent with the reactions of $Os(CO)_4(\eta^2\text{-}C_2H_2)$ with phosphines, the first step of the reaction is CO substitution by the free phosphine end of $Ru(CO)_4(\eta^1\text{-dppm})$ to give the intermediate, $RuOs(CO)_7(\eta^2\text{-}C_2H_2)(\mu\text{-dppm})$ (**16**). Due to the four electron destabilization, this species then undergoes CO insertion at the osmium center to generate the osmacyclobutenone species $(\mu\text{-dppm})Ru(CO)_4Os(CO)_3\{\eta^2\text{-}C_2H_2C(O)\}$ (**17**). It is noteworthy that the $\{Ru(CO)_4P\}$ unit in species **17** acts as a two electron donor ligand to the osmium center. Intermediate **17** undergoes further transformation to the dimetallacyclopentenone species, $RuOs(CO)_6\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2H_2C(O)\}(\mu\text{-dppm})$ (**15**), by opening of the osmacyclobutenone ring of compound **17**. Finally, species **15** undergoes facile CO dissociation to generate dimetallacyclopentenone compound **13**, wherein the alkene moiety is coordinated to the ruthenium center. It was found that CO dissociation occurs specifically from the carbonyl *trans* to the acyl group in compound **15**. This is attributed to the strong trans effect of the acyl group.

Finally, reactivity studies (Chapter 6) of the metallacyclic complexes demonstrate that both osmacyclobutenone $Os(CO)_2\{\eta^2\text{-}C_2H_2C(O)\}(\eta^2\text{-dppm})$ (**10a**) and osmacyclopentenedione $Os(CO)_2\{\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta^2\text{-dppm})$ (**12**) undergo facile alkylation reactions to yield the corresponding Fischer-type carbene compounds, $[Os(CO)_2\{\eta^2\text{-CHCHC(OMe)}\}(\eta^2\text{-}$

dppm)][SO_3CF_3] (**22**) and [$Os(CO)_2\{\eta^2$-C(O)CMeCMeC(OMe)\}(η^2-dppm)][SO_3CF_3] (**23**). More interestingly, thermolysis of the dimetallacyclic compound **13** generates compound $OsRu(CO)_5\{(\mu$-$PPh_2PCH_2P(Ph)C_6H_4CMe\}$ (**24**).

In summary, the results of these studies clearly demonstrate the importance of four electron interactions in determining the reactivities of $M(CO)_4(\eta^2$-alkyne) complexes towards CO substitution, CO insertion, and condensation reactions. Monitoring the formation of the obtained metallacycles provided insights into the related condensation reactions of $M(CO)_4(\eta^2$-alkyne) with other transition metal carbonyl complexes. Since most of these studies were aimed at understanding the reactivities of $M(CO)_4(\eta^2$-alkyne) complexes towards nucleophiles and elucidating the reaction mechanisms for formation of metallacycles, future work in this area should be directed to further develop the organic chemistry of these metallacycles and thereby increase our knowledge of the potential role metallacycles play in heterogeneous and homogeneous catalysis.

References

(1) Burn, M. J.; Kiel, G.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989,** *111*, 6850.

(2) Gagne, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561.

(3) Takats, J. *J. Cluster Sci.* **1992,** *3*, 479.

(4) Washington, J. Ph. D. Thesis, University of Alberta, 1994.

(5) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.

(6) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.